THE ELECTROKINETIC BEHAVIOUR OF SUSPENSIONS.

THESIS

presented by

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INTRODUCTION

When a solid and a liquid are in contact, an electrical double layer is established at the interface. This layer is formed by the unequal distribution of potential-determining ions between the phases and is, therefore, a separation of charges. Because of this separation, a potential exists at the interface, the zeta-potential.

If an external potential is now applied to the system, various electrokinetic phenomena may be observed.

(1) If the solid is fixed, e.g., a diaphragm, liquid migrates, a phenomenon known as _electro-osmosis_ or _electro-endosmosis_. Additionally, if the solid is porous, the liquid will move through it towards one or other electrode, a process designated as _electrodialysis_.

(2) If the solid is free to move, e.g., particles in suspension, it will migrate through the liquid, this movement being termed _cataphoresis_ or _electrophoresis_. Further, if the solid particles are permitted to reach the electrode, they may be deposited upon it, giving _electrodeposition_.

In the reverse manner, the mechanical movement of one phase through another has the complementary effect of setting up a potential difference.

(1) If liquid is forced through a porous solid, acting as a diaphragm, the potential set up is known as _streaming potential_.

(2)/

(2) If a solid is caused to move through a liquid, e.g., under gravitational forces, the potential which arises is called sedimentation potential.

The main applications of electrokinetic phenomena may be summarised under separate headings.

Electro-osmosis.

This has been applied to the removal of water from substances, such as peat, which have very high moisture contents. It has also found applications in extraction processes for water-soluble materials in the sugar industry and in impregnation processes such as the tanning industry.

Electrodialysis.

The interposition of a diaphragm, or diaphragms of a porous nature converts electro-osmosis to electrodialysis and in this form the action has found a great many uses. A large number of materials have been purified by the removal of electrolytes and of inorganic impurities forming the ash of the material. Separations or fractionations of mixtures have been achieved.

Electrophoresis.

The main applications of this phenomenon have been found in the field of protein chemistry and in biology. Separations of amino-acids and protein mixtures, both qualitatively and quantitatively, have been accomplished and it has been made possible to obtain electrophoretic patterns of sera and similar biological fluids.

Electrodeposition.

The chief use of this form of deposition has been the formation of surface coatings on objects which are made the negative or positive electrode of the system, depending on the direction of migration of the solid particles. Rubber has been deposited in this way, as have inorganic insulating coatings. Another application is the removal of finely divided conducting materials, e.g., magnesium, from organic liquids.

The present work was initiated with a view to finding applications of these phenomena which would either improve the quality of some of the natural resources of the country or provide new methods of obtaining industrially useful materials from them.

The experimental section of the thesis is divided into two main sections, inorganic and organic. The first deals with the mineral, dolomite, and the second with seaweed, and related products, and fish albumen, the aim and general scheme of the work being described at the beginning of each section.

Definitions of electrokinetic phenomena.

Electrophoresis may be defined as the movement of small charged particles in suspension in a liquid under the influence of an applied electric field.

Electro-osmosis is the movement of charged layers of a liquid in contact with a solid, due to the influence of an applied/

applied electric field.

Electrodialysis is the passage of a liquid through a porous membrane under the influence of an applied electric field.

Streaming potentials are potentials set up when a liquid is forced through a porous membrane, this effect being the complement of electrodialysis.

Sedimentation potentials are potentials which arise from the settling of small particles from suspension in a liquid.

All of the above phenomena have as their origin the charge which exists at a solid-liquid interface.

The cause and nature of the electrical charge at a solid-liquid interface.

The charge which exists at a solid-liquid interface is caused by the establishment of an electrical double layer on the surface of the solid and in the layer of liquid with which it is in contact. This electrical potential arises from an unequal distribution of the potential-determining ions between the two phases. The reasons for this unequal distribution have been under discussion for many years and a complete review of the theoretical literature regarding electrokineticsis given in the following section.

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SURVEY OF THEORIES
OF ELECTROKINETICS.

The first observations on electro-osmosis and electrophoresis were made by Reuss (1808) who found that a plug of powdered quartz in the bend of a U-tube caused a rise in the liquid level in the arm which contained the negative electrode, when a potential was applied. This was caused by electro-osmosis. In a further experiment, Reuss used a block of clay covered with sand into which were sunk two glass tubes containing electrodes. On the application of a potential difference there was no liquid flow but clay particles moved towards the positive electrode. This was an electrophoretic migration.

In 1846, Napier (1) showed that acids and salts reduced the amount of water transported by electro-osmosis.

Wiedemann (2) in 1852, showed that the amount of liquid transported through a porous diaphragm was proportional to the current but was independent of the area or thickness of the plate.

In 1859, Quincke (3) discovered that if a liquid was forced through a porous diaphragm, a potential difference was set up. This is "streaming potential." The e.m.f. produced when water was forced through a diaphragm was found to be independent of the size or thickness of the diaphragm and of the amount of water forced through, but it was dependent on the pressure used. Alcohol raised the potential while salts lowered/

lowered it. It was found that practically every substance became charged when placed in contact with a liquid, especially if the liquid were water. Quincke assumed that the capillary wall of the solid became negatively charged and that the water next to it became oppositely charged, setting up a difference of potential between the two surfaces.

It was found, however, that water could be made to travel towards either electrode, depending on the solid used and Coehn (4) postulated that when two non-miscible substances were placed in contact, one of them being a pure liquid, the substance with the higher dielectric constant is positive against the substance with the lower. Thus, almost every solid would be electro-negative against water.

Helmholtz (5) combined the laws of electrostatics and hydrodynamics, making the following assumptions:

(a) The liquid was oppositely charged to the rigid wall, forming an electrical double layer.

(b) The thickness of the double layer was very small, being of about molecular proportions.

(c) The layer of water molecules in contact with the wall was immovable. The rest of the molecules in the liquid near the wall and in the double layer (the strongly adsorbed layer) were movable and subject to the ordinary laws of friction for normal liquids.

(d) Only laminar flow of liquid could occur.

(e) The external potential difference was simply superimposed on the potential difference in the double layer itself.

(f) The wall was an insulator and the liquid an electrolytic conductor. Then, if σ were the charge density on the wall and δ the mean electrical thickness of the double layer and D the dielectric constant of the media between the two layers, the potential across the layers ζ, was given by

$$\zeta = \frac{4\pi.\sigma.\delta}{D}$$

Freundlich (6) examined the effect from the point of view that if the solid were fixed and the liquid free to move, the application of a potential would cause a continuous displacement of liquid along the surface of the solid, with steady re-establishment of the double layer. He showed that for a capillary tube:

$$V_e = \frac{\pi.r^2.\epsilon.E.D.}{4.\pi.\eta.\ L.}$$

in which V_e is the amount of liquid transported electrically through a single capillary tube in unit time.

E is the fall in potential through the capillary tube.

D is the dielectric constant of the liquid concerned.

η is the viscosity of the liquid.

ϵ is the potential of the double layer at the interface.

L/

L is the length of the capillary.

r is the radius of the capillary.

For a porous diaphragm, if it might be considered as a bundle of capillary tubes, $\Sigma \pi . r^2 \propto q$ (area of the diaphragm)

$$\text{and } V_e = \frac{q . \varepsilon . E . D .}{4 \pi . \eta . L .}$$

Since $E = IR$ and $R = \frac{L}{\gamma . q}$ where γ is the specific conductivity of the liquid, then

$$V_e = \frac{\varepsilon . I . D .}{4 . \pi . \eta . \gamma .} = \text{constant} \times I.$$

The amount of electro-osmosis was, therefore, independent of the size of the diaphragm.

In addition, Freundlich noted that equilibrium would be reached when the transport of liquid in one direction by electro-osmosis was balanced by the resultant hydrostatic pressure moving the liquid in the other direction. Poiseuille's law holds for the latter, giving:

$$V_p = \frac{\pi . r^4 \quad P}{8 . \eta . L}$$ where P is the difference in hydrostatic pressure between the ends of the tube.

Equating V_e and V_p at equilibrium gives:

$$P_e = \frac{2 . \varepsilon . E \ D}{\pi . r^2}$$ where P_e is the hydrostatic pressure produced by electro-osmosis in a narrow capillary.

This could not be applied to a diaphragm, since Poiseuille's law holds only for narrow capillaries. However, as long as the average size of the particles of the diaphragm remained/

remained constant, the mean cross-sectional area of the pores could be regarded as unchanged and πr^2 replaced by a constant k.

$$\text{Thus} \quad P_e = \frac{2 . \varepsilon . E \, D}{k} = K_o E$$

i.e., for a given liquid, the hydrostatic pressure produced by electro-osmosis through a given diaphragm of definite porosity etc. is proportional to the total fall in potential through the diaphragm and is independent of the dimensions of the diaphragm.

The effect of dissolved substances.

Porrett (7) observed that dilute sulphuric acid reduced the flow of water by electro-osmosis to almost zero.

Daniell (8) noted the differences of liquid level across a diaphragm produced by electro-osmosis at 30 volts. He found that a solution of sodium phosphate gave a difference of 2 inches, sodium sulphate 1.5 inches, distilled water 1 inch, dilute sulphuric acid 0.25 inch and stronger sulphuric acid no difference.

Wiedemann (2) postulated that the greater the resistance of the liquid, the greater was the amount transported under the same conditions of current strength.

Quincke (9) forced water containing various solutes through diaphragms. He found that no current was produced when dilute sulphuric acid was forced through a porous earthenware diaphragm/

diaphragm. Alcohol increased the current produced while caustic soda and copper sulphate weakened the effect. Using powdered sulphur as a diaphragm, he observed that both nitric acid and sodium chloride reduced the current compared to distilled water. Tannin and soap both increased the current obtained using powdered glass. Mineral waters gave less current than distilled water. He summed up his findings by saying that the addition of acids and salts to distilled water reduced the intensity of the current until it was no longer noticeable. With aqueous alcohol, which gave an increased e.m.f., it was noted that the exit liquid was appreciably richer in alcohol than that entering. Dissolved salts always produced a marked decrease in electro-osmosis, even material from the glass of the containing vessel affecting it.

In all the above cases, flow was from anode to cathode but Quincke noted flow from cathode to anode using turpentine.

Gernez (10) observed a creeping action of a water film wetting the inner surface of a capillary tube on the application of a potential difference. Movement was always towards the cathode and was only observed in the film contingent to the glass surface. He also noted that acids, alkalis or neutral salts all reduced the speed of transport.

Perrin (11) designed a new type of electro-osmometer, in which different solids were used as diaphragms in the form of/

of powder. The diaphragm was formed in one limb of a U-tube and electrodes inserted immediately above and below it. A calibrated capillary tube led off from the U-tube above the upper electrode and differences of level in this tube were measured. Using this apparatus, he found that increase of temperature gave an increase in the volume of liquid transported and assumed the effect was similar to that on fluidity.

Coehn and Raydt, (12) however, using the rise in a capillary tube, which is independent of viscosity, found a small negative coefficient with temperature, of the approximate order of the (negative) coefficient of dielectric constant.

Cameron and Oettinger (13) gave confirmatory evidence by measuring diaphragm potentials, which they found to decrease slightly between 21 and 31°C.

Cruse, (14) using a porous earthenware diaphragm, found that the electro-osmosis of distilled water rose to a maximum between 35 and 40°C., above which it decreased rapidly at first and then more slowly.

Perrin (11) came to the conclusion, regarding dissolved substances, that electrolytes alone influenced electro-osmosis, ions being the active agents. Traces produced big effects, the activity of different ions varying greatly. The degree of acidity or alkalinity of the solution was an important factor.

Using diaphragms of insoluble chromic chloride, alumina, carborundum, sulphur, gelatine, graphite, etc., he found that acids/

acids flowed to the anode while alkalis flowed to the cathode. These results led Perrin to state that in the absence of polyvalent radicals, every non-metallic substance is positive in an acid liquid and negative in an alkaline liquid.

Briggs (15) pointed out that this ignored the specific effect of the diaphragm material. Perrin found exceptions to his rule, however, e.g., both acids and alkalis flowing to the cathode through cotton wool (cellulose). As the strength of the acid increased, the flow decreased until it became zero. Perrin modified his previous statement, saying that the electrical potential of any surface in aqueous solution was invariably increased by the addition of a monovalent acid and decreased by the addition of a monovalent base. He considered that the explanation was a question of the difference of solubilities in water, i.e., change of ion content, especially if giving a change in pH. Briggs said that preferential adsorption of ions on the diaphragm, a property characteristic of the diaphragm, must also be considered. Perrin was of the opinion that if the diaphragm were positive, anions were more active than cations and vice versa. Anions lowered the positive charge on the diaphragm causing a falling off in the rate of flow, the effect becoming greater with higher valency of the active ion. Cations acted similarly with negative diaphragms.

Freundlich (16) found the concentration of salt in millimols/litre required to produce a half-value of the electro-osmotic effect and showed that $Br' > SO_4'' > Fe(CN)_6'''$ for the concentration required. Similarly $Na^+ > Ba^{++} > La^{+++}$.

Perrin showed that reversal of interface potential could be obtained using polyvalent ions of unlike charge to the diaphragm. This showed that every diaphragm tended to become positively charged against an acid solution and negatively charged against an alkaline solution. Every ion of unlike sign tended to neutralise the charge on the diaphragm, the tendency increasing rapidly with increasing valency of ion.

Baudoin (17) used methyl alcohol and found that alkali alcoholates in alcohol were equivalent to alkali hydroxides in water. Acids had the same effect in alcohol as in water and polyvalent ions conformed to Perrin's theories.

Larguier des Bancels (18) used textile materials as diaphragms and found that wool > silk > cotton with reference to the electro-negative charge against distilled water. In acid solution, silk showed reversal, the others remaining electro-negative against dilute hydrochloric acid. Polyvalent ions again behaved according to Perrin's rule. Wool dyed with basic dyes was much less electro-negative against water than undyed wool.

Bose-Guillaume (19) confirmed Perrin's rules. Two wires, one/

one covered with a very thin coating of a porous material, such as gelatine, were placed in a solution and the coated wire given a sudden twist. A momentary e.m.f. was produced. This was caused by the squeezing of liquid through the pores of the coating material, giving a special case of Quincke's diaphragm currents. If the porous coating was negative against the liquid, the coated wire became negative with respect to the uncoated wire, producing a momentary current. Using platinum wires coated with gelatine or fire-hardened clay, it was shown that against an alkaline solution the coated wire was negatively charged, in the absence of disturbing polyvalent radicals. Ions such as Ba^{++} and La^{+++} neutralised the negative charge to a great extent. The polyvalent anion $Fe(CN)_6'''$ increased the negative charge, more than neutralising the effect of the K^+ ions. Against hydrochloric acid, the coated wire was positively charged and polyvalent anions reduced the e.m.f. $Fe(CN)_6'''$ was very active, producing a marked reversal.

Ascoli (20) carried out electro-osmotic experiments with liquid ammonia and found that alumina diaphragms were positive against the pure liquid but became negative when sodium was added.

Morse and Horn (21) observed strong electro-osmosis through a porous cup in which they were depositing, electrochemically, a copper ferrocyanide membrane. The liquid in the/

the cup rose with a rapidity which increased with the dilution of the solution and the intensity of the current.

Frazer and Holmes (22) studied very dilute solutions of alkali and alkaline earth nitrates and came to the conclusion that the amount of osmosis of various salts with a common anion varies approximately inversely as the velocity of the cation divided by its valence. Their method was to measure the amount of osmosis of various 0.001N. solutions compared to potassium nitrate of equal strength, the amount with which was taken as 100. In all cases where neutral salts were used, the usual flow to the cathode was observed, but reversals were found with solutions of common acids. Such a reversal was found using a solution of acetic acid, which moved faster than hydrochloric acid. Perrin had believed that the rate of flow of acids with a monovalent anion was an approximate measure of their dissociation. Briggs suggests that a theory of preferential adsorption will explain this effect.

Coehn (23) made experiments using a Pukall filter. He found that solutions of caustic potash and sulphuric acid always flowed to the cathode. Nitric acid flowed to the anode except at concentrations of less than 1 mg.mol/litre. Acetic acid did not show reversal until 200 mg.mol/litre had been exceeded. Neutral sulphate solutions flowed to the cathode under/

under all circumstances and alkali nitrates did the same. Solutions of heavy metal nitrates, however, flowed to the anode, except when extremely dilute.

Barratt and Harris (24) used diaphragms of gelatine, parchment and agar and found the usual acid-alkali reversal with gelatine only. Parchment, being cellulosic in nature, can be expected to give no reversal. Using a diaphragm of 10 per cent. gelatine, Barratt and Harris found that solutions of the following salts flowed to the cathode as shown.

$Na_2SO_4 > NaOH > NaNO_3$, the rate increasing with concentration. Solutions as follows flowed to the anode in the order given $Al(NO_3)_3 > Cu(NO_3)_2 > HNO_3$.

Using parchment, solutions always flowed to the cathode, the order being as follows:

$$Na_2HPO_4 > Na_2SO_4 > NaOH > NaCl > HCl > CuCl_2 > AlCl_3.$$

The chlorides of copper and aluminium gave rates of flow which rose to a slight maximum with increasing concentration, but soon fell almost to zero, even when the amount of salt present was actually very small. With agar diaphragms, as the concentration of dissolved electrolyte increased, the osmosis rate passed through a distinct maximum in every case. As in the previous examples, the rate of flow to the cathode decreased in the order given below:

$$Na_2HPO_4 > Na_2SO_4 > NaOH > NaCl > HCl > CuCl_2 > AlCl_3.$$

Elissafoff (25) used a single capillary tube placed between/

between the poles of an electrostatic machine, the tube being glass or quartz. The tube was filled with a neutral solution except for a small air bubble. On application of an external electric field, a film of liquid was dragged along the surface of the tube and around the air bubble until a drop collected, finally, at one or other end of the tube. Comparing solutions with pure water, he obtained an empirical relationship between osmosis and concentration.

$$\Delta V\bar{e} = R \cdot \log_e C + \gamma$$

where $\Delta V\bar{e}$ is the lowering of osmosis by adding the salt to water, C is the concentration of the solution and R and γ are constants.

Glass and quartz were found to be strongly electro-negative and were affected by cations in most cases. The valency rule held for alkali and light metals but failed for heavy metals and certain organic cations. No reversal was observed with acids but the solutions were never stronger than 0.0001N. Reversals were obtained, however, with certain salt solutions. Thorium nitrate solutions of sufficiently high concentration caused glass to become positive as also did basic dyes. In all cases, the addition of electrolytes produced a decrease in the rate of electro-osmosis. Elissafoff found, however, that caustic potash gave an increased flow to the cathode, and concluded that there seemed to be no rigid rule that dissolved substances always reduced the contact electrification/

electrification, just as there seemed to be no rigid relationship between valency and contact potential.

Theories of contact electrification and adsorption.

Wiedemann (2) believed that an electric current exerted a tractive action on liquid contained in a capillary tube and that the liquid was carried thus from anode to cathode regardless of the material forming the walls.

Graham (26) and Breda and Logemann (27) opposing this, showed that no transport of liquid occurred unless a diaphragm or its equivalent was present. Quincke (3) and Helmholtz (5) put forward the electrical double layer theory, which will be dealt with later, along with more recent theories in that connection.

Coehn's (4) rule extended this theory. Briggs (15) made a comparison with the Nernst theory of solution. This theory holds for the special case of a metal in contact with its own ions. Briggs drew an analogy for non-metallic solids. Every solid dissolved in water to a certain extent and the electrical double layer might be supposed to be formed by differences in the rates of ion diffusion, producing a separation of charges. He pointed out that this explanation could not be correct for the case of a solid immersed in a pure liquid, unless the liquid remained unsaturated with respect to the solid or, alternatively, that fresh liquid was constantly supplied. The electrical charge did not disappear/

disappear when the liquid became saturated with the particular solid, although the sign and intensity might change. In the case of a concentration cell, however, the potential difference at the interface existed only as long as a difference in concentrations was maintained. No permanent potential difference could possibly be produced as a result of unequal ion mobilities. Briggs suggested adsorption as offering a rational explanation.

The contact potential between a solid and a solution was a more complex problem. Perrin (11) offered the explanation that since hydrogen and hydroxyl ions were abnormally mobile, they must be correspondingly small and thus be able to crowd to the surface of a solid more closely than any other ions, making the solid positive in acid solutions and negative in alkaline solutions.

Briggs claimed that this was a case of selective adsorption. The extent to which selective adsorption depended on the relative mobilities of ions was not so clear. The work of Frazer and Holmes (22) seemed to indicate a relationship where the ions were very similar chemically. Cameron and Oettinger (13) refer to Rutherford who found that if an ionised gas were passed through a metallic tube, the tube became electrified positively or negatively according to the sign of the charge of the more rapidly diffusing ion.

Perrin (11) observed that a solution of lithium bromide failed to charge a chromic chloride diaphragm negatively although bromine ions were twice as mobile as lithium ions. Briggs (15) suggested/

suggested that the ions produced in solution by the chromic chloride might explain this. Further, if the relation held between selective adsorption and ion mobilities, the tendency to reduce the positive charge on the chromic chloride would be greater with lithium bromide than with potassium bromide.

Frazer and Holmes'(22) data confirmed this to a certain extent. Haber (28) was of the opinion that in the case of glass against water, the solid was essentially a hydrogen electrode and the magnitude of the potential difference would depend on the concentration of hydrogen ions in solution.

Cameron and Oettinger (13) following this, experimented with the e.m.f.'s produced by forcing acids and alkalis through glass capillaries but their findings were inconclusive.

Freundlich (16) objected to the theory of Haber on the grounds that electro-osmosis did not depend entirely on hydrolysis of the dissolved solute as it should do if the concentration of hydrogen ions was the only factor. He went on to study the relationship of adsorption to electro-osmosis. He had already shown the relation between the stability of suspensions and adsorption and had pointed out the validity of the Schulze rule of valency for adsorbed light metal cations and the ordinary anions. He discovered that many organic anions were exceptions to the Schulze rule and applied this to show that these ions were also exceptions to Perrin's valency rule.

He/

He called the difference of potential between a solid and a solution the "adsorption potential" and stated that if the cation was adsorbed to a greater extent than the accompanying anion, the solid would become positively charged and if it were employed as a diaphragm, electro-osmosis would occur from cathode to anode. For the case of a solid immersed in pure water, he postulated selective adsorption of ions already present in the water or produced by slight solution of the solid itself. When preferential adsorption occurred, the actual number of ions adsorbed was very small, since the charge on a single ion was relatively large and the electrical double layer that was established opposed any further spacial separation of positive and negative ions.

Freundlich (29) modified his original theories, stating that the contact potential of the diaphragm depended on the nature of the material of which it was composed (upon differences of solution tension of ions thrown out) and was only indirectly affected by adsorption. Briggs, (15) however, thought that while the nature of the diaphragm was a factor in contact potential, the power of the solid to adsorb selectively the ions present in the liquid from the start or produced by the solid dissolving was the important thing.

Frazer and Holmes (22) had a different theory based on the theory of solvation. If the hydration of the cation were greater than that of the anion, the liquid should be carried from/

from the anode to the cathode, as was found to be the case with neutral salts of alkalis against earthenware. Since the mobility of an ion may be regarded as an inverse measure of the hydration, it would be expected that a strong flow to the anode in acid solution and to the cathode in alkaline solution would be obtained. It was confirmed that with a series of salts having a common anion, the amount of flow to the cathode increased with decreasing ionic mobility.

Barratt and Harris (30) thought that the flow of liquid in electro-osmosis was determined by the movement of the ions contained in the liquid at the surface of contact with the solid. These ions caused a passive movement of molecules of liquid in the same direction. They found that the narrower the interval between the particles of which the diaphragm was composed, the more marked was the movement of liquid. They also stated that the more numerous the ions in the liquid portion of the double layer, the greater was the flow of liquid at first, although with continued increase in the number of ions, a diminution of liquid flow later occurred. Hydration of the ions was also thought to be a factor. They postulated that the electric current was carried through the diaphragm by those ions not in the double layer and, if these ions were hydrated, the flow would be greater by a certain amount, dependent on the relative hydration of anion and cation and their transport numbers/

numbers.

Briggs (15) thought that this theory was incorrect and suggested that ion mobility was only important as far as it was related to adsorption.

Bancroft (31) stated that the sign of the charge on the diaphragm was dependent on the relative adsorption of the cation and the anion, being positive if the cation was adsorbed to a greater extent than the anion and negative if the reverse held.

Briggs (15) postulated that solid surfaces were capable of adsorbing ions preferentially. Every solid had a specific adsorbing power for a given ion, this power depending on the specific surface of the solid, the temperature, the concentration of the particular ion in solution and upon other ions present or adsorbed previously by the solid. There was little electro-osmosis when the ion content of the liquid was small since there would be little ion adsorption. Non-dissociated liquids showed little electro-osmosis. Electro-osmosis of pure water was to be explained by ionisation of the water and preferential adsorption of ions dissolved from the solid itself. Since the majority of solids were negative against water, he postulated that hydroxyl ions were adsorbed preferentially to hydrogen ions. There were thus two factors to be considered:

(1) The specific adsorption of hydrogen and hydroxyl ions produced by the dissociation of the water.

(2)/

(2) The solution of the solid itself, which although extremely small might produce ions which were strongly adsorbed.

He summarised his theories thus:

(1) Electro-osmosis depends on the preferential or selective adsorption of ions and is influenced only by those ions adsorbed by the diaphragm.

(2) Any circumstance or condition which changes the adsorption produces an effect on the electro-osmosis, which varies for any given surface, therefore, with the condition of the surface, with the relative and absolute ion concentrations, with the temperature etc.

(3) The direction of electro-osmotic flow indicates the sign of the charge on the diaphragm, negative if towards the cathode and positive if towards the anode. No flow of liquid indicates an iso-electric condition. The rate of flow is an indication of the intensity of the charge on the diaphragm, when the potential gradient through the diaphragm is constant.

(4) The diaphragm tends to become positive by selective adsorption of cations and negative by the selective adsorption of anions.

(5) The charge produced by an adsorbed ion is neutralised more or less by the addition of an adsorbed ion of opposite charge, the effect increasing with increasing concentration of the added ion.

(6)/

(6) Electro-osmosis measures the tendency of a solid to form an electrical suspension in a given liquid but does not measure the tendency to form a non-electrical suspension, such as is produced by adsorbed solvent, solute or neutral colloids.

Porter,(32) following the work of Helmholtz, derived equations for electro-osmosis.

$$\zeta = \frac{4.\pi.\eta.U}{DRI} = \frac{P.\pi^2.r^4}{2D.R.I.L.}$$

where U = amount of liquid transported, η = viscosity, P = pressure gradient, r = radius of capillary, R = resistance and I = current.

He took the point of view regarding electrophoresis of ionic migration, that colloidal particles behave as individual ions of high molecular weight and charge and show a migration rate in an electric field that approximates to that of common ions except that of hydrogen and hydroxyl ions. Size has little effect on the rate, since a larger radius corresponds to a larger surface with a larger charge, counteracting the effect of increased viscosity. Migration occurs in pure water or in solutions of electrolytes. Many colloids are positive in acid solution and negative in alkaline solution. The point of view is similar to that used in electro-osmosis, the double layer in this case being on the surface of the particles. An electrical field will tend to displace negatively charged particles with respect to positively charged liquid. Since the particle/

particle is more free to move than the liquid, which is retarded by its own viscosity, the solid migrates. He showed that:

$$c = \frac{-E}{6.\pi.\eta.}\,\frac{q}{r} = \frac{-E.D.\zeta.}{6.\pi.\eta.}$$

where c = velocity of particle, E = field strength, r = radius of particle, η = viscosity, q = charge on particle, D = dielectric constant, ζ = zeta potential.

If q is directly proportional to r, c is independent of particle size. Electrophoresis is the opposite of electro-osmosis and Porter derived the equation

$$\zeta = \frac{-4.\pi.\eta.v}{D.R.j}$$

where v = electrophoretic velocity and j = current density. Migration did not depend on the shape of the particle.

MacDougall (33) dealt with streaming potential, stating that the streaming potential set up was sufficient to send an equal current in the opposite direction. He derived the equation:

$$\zeta = \frac{4.\pi.\eta.k.S}{P.D.}$$

where k = specific conductance of the liquid and S = streaming potential. The streaming potential is independent of the dimensions of the capillary.

Ettisch and Zwanzig (34) found that the above equation broke down at higher pressures but approached a limiting value. This/

This showed that the double layer was broken closer to the solid surface, the greater the mechanical force applied.

As far as sedimentation potential was concerned, the e.m.f. was formed by the solid moving relative to the liquid and dragging part of the double layer with it. The general equation for streaming potentials should, therefore, be valid in this case, where P = pressure difference produced by the falling particles. For small spheres P = apparent weight of the particles.

Horwitz (35) considered the assumptions made in dealing mathematically with electrokinetic phenomena.

(1) Dielectric constant.

Helmholtz used the value 1, assuming that the thickness of the double layer was such that no molecules could occupy the intervening space, an assumption no longer tenable on the basis of the modern diffuse double layer theory. Rideal (36) used a value of about 7. In most cases the ordinary dielectric constant of the solvent was used. It has been shown that the value of the dielectric constant of water may vary from very low values (approximately 1) to the normal value of about 80, under varying conditions of frequency and under high intensity electric fields. Since the double layer builds up a large electric field in its immediate vicinity, it would be expected to change the value of the dielectric constant.

Bull and Gortner (37) gave three reasons why the value of the dielectric constant in the double layer should be different from the value in the bulk of the liquid.

(a) There is a tendency for molecules to become orientated at a surface, the potential contributed by this having a great effect upon the dielectric constant and, in the double layer, will tend to increase the value.

(b) It has been found that a material with a higher dielectric constant tends to displace other material with lower dielectric constant from an interface. This is especially important with organic liquids of low dielectric constant, because traces of water will be adsorbed almost completely at the surface, raising the value of the dielectric constant and producing effects quite out of proportion to the actual amount of water present. With salt solutions the value of D is greatly lowered with small concentrations but increases to values higher than that of pure water at greater concentrations.

(c) Near the ions of an aqueous salt solution there exist saturation effects that become greater as the ion is approached. The more concentrated the salt solution, the more important becomes the effect since the thickness of the double layer is decreased, bringing the ions of the double layer closer together. This tends to decrease the value of the dielectric constant.

They therefore suggest that the use of the dielectric constant in electrokinetics be discontinued and results expressed as electrical moment, which is the charge per unit area of the double/

double layer X the thickness.

Kallman and Dorsch, (38) as a result of experiments with organic liquids and water, stated that the dielectric constant of very thin films showed a maximum deviation from the normal of only 0.5 per cent.

(2) Coefficient of viscosity.

It is probable that the coefficient of viscosity of a solution in bulk is the same as that between the movable and immovable parts of the double layer, since both are composed of highly solvated ions. It is possible, however, for ions of a salt solution to be adsorbed into the interface increasing the effective concentration in that region and changing the value of the coefficient of viscosity. Evidence indicates that adsorbed molecules are under tremendous pressure which will certainly change their shape and consequently produce a change in viscosity.

The experiments of Bull and Moyer (39) showed that the viscosity of water was a function of the width of narrow slits. Water exhibited rigidity when placed between glass surfaces less than 150 microns apart, the effect vanishing at greater distances.

Bull and Gortner, (40) using diaphragms of fine quartz particles, found a marked decrease in streaming potential which became apparent with particles slightly below 200 microns in diameter and became increasingly important as the size decreased/

decreased. The effect was also due to the smaller capillaries produced. Slippage at the surfaces was not considered important.

(3) Specific conductance.

This refers to the liquid, as it is assumed that no surface conductance occurs on the solid. If the liquid has a low conductance, however, surface conductance is important. It is negligible with salt solutions. When it is taken into consideration, a term must be introduced containing the dimensions of the tube. This can be eliminated in experimental work by determining the cell constant of the diaphragm with a standard solution of potassium chloride.

(4) Thickness of the double layer.

Helmholtz assumed that this was constant; but this was not so. This led to the transformation from the parallel plate theory of the double layer to the diffuse double layer theory, in which one layer is attached rigidly to the solid wall while the other extends for some distance into the liquid. As the concentration of electrolyte increases, the part of the double layer in the solution is pressed closer to the rigid layer, decreasing the thickness of the double layer.

(5) Other quantities.

Electrokinetic velocities are such that motion is streamlined. There are thus limits to the capillary size and pressure used to avoid turbulent flow. Cruse (41) and Gee and Harrison (42) found that the zeta potential appeared to have a temperature/

temperature coefficient, maximum at 35-40°C. for clay, wool, cotton and silk.

Types of potential at an interface.

(a) Diffusion potential.

This is set up with two solutions, containing different concentrations of the same ions in the same solvent, and is due to unequal mobility of the ions. The effect decreases with time as the concentrations of the two solutions approach equality.

(b) Thermodynamic potential (ε)

This exists at the boundary of a solid and a liquid and is a logarithmic function of the concentration of ions of the solid in the liquid.

$$\varepsilon = \frac{R.\ T.\ \log_n . c.}{\mu\ .\ F}$$

(c) Distribution potential.

This is set up at the boundary of two immiscible liquids in which individual ions have different "solubilities." The activity of the salt is the same in both phases, but not the individual ion activities. The difference is compensated for by a potential.

$$\pi = \frac{R.\ T.\ \log_n .}{F} \sqrt{\frac{\gamma A}{\gamma K}}$$

where γA = the distribution coefficient of the anion of AK, and

γK = the distribution coefficient of the cation of AK.

(d)/

(d) Membrane potential.

This occurs at the surface of two solutions, containing the same solute but separated by a semi-permeable membrane.

(e) Adsorption potential.

This is caused by the adsorption of ions at an interface, when the activities of the ions are variously affected and a potential set up.

Thermodynamic and electrokinetic potentials.

The thermodynamic potential is measured perpendicular to the interface, the current flowing across the double layer, while the electrokinetic potential is measured tangentially to the interface, the current flowing parallel to the double layer. The latter is the work necessary to take unit positive charge from the interior of the liquid up to the strongly adsorbed layer, while the former is the work necessary to take unit positive charge from the interior of the liquid to the interior of the solid.

In electrokinetics, movement takes place against a thin film of liquid rigidly attached to the solid. It is assumed that the potential drop is greatest in a thin, many-molecular layer between the solid and the interior of the solution, but what is effective is only the potential drop between the strongly adsorbed layer (not the rigid layer) and the interior of the solution and this is what is measured as zeta/

zeta-potential. The zeta-potential is usually less than 0.1 volt while the thermodynamic potential is often as large as 1 volt. The electrokinetic potential is part of the thermodynamic potential but is, otherwise, independent of it and is often of the opposite sign. Using a glass-water interface, Freundlich and Ettisch (43) found that if the electrokinetic and thermodynamic potentials are measured for dilute solutions of electrolytes, the former exhibits maxima and minima, while the latter falls continuously for all salts with increasing concentration. In the same way, Abramson (44) measured, at a definite pH, the electrokinetic and thermodynamic potentials of thin films of adsorbed protein on glass surfaces, having different iso-electric points. It was found that the former was dependent on the plane of shear and was fixed by the ions at that point, while the latter was independent of the adsorbed layer and was the same for all films.

Structure of the double layer.

The non-identity of the electrokinetic and thermodynamic potentials led to the theory of the diffuse double layer. The Helmholtz concept assumes that the opposite but equally charged layers are at molecular distances from each other. In electrokinetic displacements, shear takes place between the layers of positive and negative charges. In this case all the potential drop must occur exclusively in the rigidly adsorbed layer

close/

close to the wall, which would mean that the electrokinetic and thermodynamic potentials were identical.

Gouy (45) supplied a modification by considering that the ions of the double layer were subjected to two sets of forces, an electrical force tending to make them accumulate at an interface and diffusion or heat motion tending to re-establish the original condition of uniform distribution of positive and negative ions. The diffusion tendency has little effect on the rigid layer of negative charge, since the electrical adsorption charges are so large, but the effect is considerable in the rest of the double layer, giving rise to a distribution of the cations according to the 'e' function of Boltzmann, in a manner analogous to the distribution of air molecules in the atmosphere where diffusion and gravitational potentials oppose each other. The result is an atmosphere of diminishing intensity - the diffuse double layer or ionic atmosphere. On the basis of this theory, 'd', the distance between the oppositely charged Helmholtz layers, is the distance between the rigid layer and the centre of gravity of the diffuse outer layer. This is the distance at which an infinitely thin layer of ions, having total charge equal to the outer Helmholtz layer, must be placed in order to exert the same electrical force as the real distribution.

Gouy deduced the formula

$$d = \sqrt{\frac{D.\ k.\ T.}{4.\pi\ N.\ \varepsilon^{2}.(z_1 + z_2)c_1\ z_1 \text{ or } c_2 z_2}}$$

where/

where z = valency (subscript indicating the cation or anion)

k = Boltzmann's constant.

N = Avogadro's number.

c_1 or c_2 = ionic concentration of anion or cation (in moles/cc).

D = Dielectric constant.

ε = charge on the ion.

An increase in electrolyte concentration decreases the width of the diffuse layer. With pure water, this extends a considerable distance into the liquid. As the concentration of electrolyte increases, it is pushed up closer to the other layer, reducing the zeta potential (while the thermodynamic potential need not change). This may occur to such an extent that a true Helmholtz double layer is formed or the double layer collapses entirely.

Gouy's theory is incomplete, says Horwitz, and does not agree very well with experiment. It does not predict the correct relationship of the distance across the double layer and the concentration of electrolyte. No mention is made of the adsorbability of ions, which is of great importance for capillary-electrical processes and for the phenomenon of flocculation.

To account for this, Stern (46) combined the Helmholtz double layer with the Gouy diffuse double layer. The charge near the solid resides on the rigid layer while the charge in the solution is partly present as a diffuse layer and partly as a strongly adsorbed layer at a distance of about the mean ionic/

ionic radius from the rigid layer. The potential gradient is steeper over the inner, condenser-like layer and falls off more gently over the outer portion. In some cases a twofold ionic stratification may exist before the outer layer is reached and the potential/distance curve will then show a point of inflection.

Stern's theory contains many simplifying assumptions and cannot easily be checked experimentally. It probably represents the true state of affairs more closely than that of Gouy, states Horwitz.

Mathematical treatment of the diffuse double layer.

In the original treatments of the diffuse double layer, it was assumed that the charges constituting the layer had no effect on each other. Debye and Hückel (47) showed that for concentrated solutions of electrolytes, the effect of charged ions close together was quite appreciable and they developed equations to account for it. These equations apply also to the charges constituting the double layer.

Horwitz shows that the change in zeta-potential may be due to a change in the thickness of the double layer or to a change in the number of ions adsorbed. The thickness decreases with increasing concentration of ions, especially polyvalent ions. The actual variation of the zeta-potential is ascribed to a large extent to this factor, and only to a lesser extent to the number of ions adsorbed. Zeta-potential curves may be of three types:

(a)/

(a) Having a maximum or minimum. At low concentration of electrolytes, the potential increases to a maximum and decreases towards the iso-electric point.

(b) The curve rises or falls continuously to the iso-electric point.

(c) The curves have both maximum and minimum. With increasing concentration, the curve first falls to the iso-electric point, then increases (with opposite sign) to a maximum and finally declines again. The reversal of charge at the iso-electric point is brought about at lower concentrations of electrolytes of higher valency than those of lower valency.

The theory of Stern.

Stern considered the Helmholtz and Gouy double layers to be idealised limits of the real situation. If the temperature were so low that heat motion might be neglected, the Helmholtz theory would be correct. For example, all negative ions would be arranged opposite to all the adsorbed positive ions and the entire potential drop would occur in a single double layer. With increase in temperature, part of the negative ions would leave their position at the interface on account of molecular motion and form a diffuse layer in the solution. Those ions still at the interface would still be arranged as a Helmholtz layer, but with an excess positive charge. This comprises Stern's double layer.

Horwitz developed equations for the charge densities in both parts, that in the rigid layer (σ_1) and that in the diffuse layer (σ_2). At small concentrations, σ_1 would be negligible compared to σ_2 and at infinite dilution, the ideal diffuse double layer would be obtained. The opposite effect would be obtained with increasing concentration, leading to a perfect Helmholtz double layer.

Philpot, (48) using a dropping mercury electrode, showed that Stern's theory was the only one giving a true picture of the double layer at a metal surface. The Helmholtz theory gave σ_0 ($= \sigma_1 + \sigma_2$) as a linear function of the potential of the adsorbed layer at all potentials, while Gouy's theory gave it as an exponential function of the adsorbed layer potential when both this and the concentration of electrolyte (mole fraction) were small and as a linear function of the adsorbed layer potential when the two were large.

The origin of the double layer.

Kruyt (49) stated that the origin of the double layer was to be sought in the unequal distribution of potential determining ions and this unequal distribution was due to lattice forces.

Michaelis (50) thought that the origin was first in the forces of residual valency, causing orientated adsorption. He gave the example of a dispersion of AgBr particles. If AgBr is precipitated in aqueous solution containing an excess of/

of Ag ions, a positively charged sol of $(AgBr)_xAg^+$ is formed, while if there is an excess of Br ions, a negatively charged sol of $(AgBr)_xBr^-$ is formed. At the exact equivalence point no sol is formed, and pure AgBr precipitated. Each atom in a cube is surrounded by six oppositely charged atoms, completely satisfying its affinity. At the surface of the particle, however, only five of the six possible "valencies" are satisfied, at an edge of the particle four and at a corner only three. Excess ions tend to be adsorbed at these points where unsatisfied affinities exist. If a salt such as KCl is added to a water suspension of pure AgBr, (51) selective adsorption of Cl ions takes place, since the K ion will not fit into the lattice. The K ions then form the outer layer of a double layer. The charge and electrokinetic potential will increase as long as Cl ions can be adsorbed. Beyond this point, positive ions will be forced closer to the inner layer, decreasing the size of the diffuse layer.

In this process, both the charge and distance factors of the electrokinetic equation are being decreased so that the zeta-potential is decreased and approaches the iso-electric point at which the K and Cl ions are so close together that they form a neutral adsorbed layer. With polyvalent ions, further changes occur with increasing concentration, taking the potential past the iso-electric point. A new diffuse layer

is/

is formed in which the polyvalent ion is the inner layer and chloride ions are the outer layer (as with thorium chloride). A reversal of charge thus occurs, the charge and potential increase further, reach a maximum and then decrease. The second layer behaves similarly.

Michaelis states that, secondly, forces of dissociation can cause exchange adsorption. Some polar compounds can dissociate very readily, but one of the components is incapable of existing in the dissolved state as an ion. The compound remains bound to the colloidal aggregate. This is the case with silicic acid which dissociates into hydrogen and silicate ions. The silicate ions adhere and are not dispersed. The hydrogen ions, or any positive ions are selectively adsorbed and form a double layer. The potential across the layer is proportional to the dissociation tendency which, in turn, depends on the nature of the solid and of the liquid phase.

When such a layer is treated with foreign electrolyte, the effects are very complicated. Ionic substitution, an extreme case of polar adsorption, occurs. The outer layer can be replaced by new ions and even the rigid layer may incorporate some of them. The potential may increase or decrease during the process, depending on the variation of the charge and thickness, which are affected by the valency and discharging effect of the ions in the double layer. In layers of this kind, the charge may increase while the thickness decreases or vice versa/

versa. At higher concentrations, when the double layers have become saturated with respect to the new components, the potential follows the ordinary course.

The third point made by Michaelis is that the double layer can arise from the spontaneous distribution of ions at surfaces in such cases where the boundary surfaces are unreactive chemically and do not dissociate. This is the case with cellulose and air bubbles, where there is no dissociation, and no residual valencies, yet a charge exists at the interface. This is ascribed to differences in the capillary activity of hydrogen and hydroxyl ions, assuming that hydroxyl ions are more capillary active than hydrogen ions and could thus come closer to the surface, thereby creating a potential difference.

Rideal (52) states that there are two theories of electrokinetic phenomena. The first is based on the work of Pauli. A colloidal particle must be ionogenic and can be regarded as a large multivalent ion, the ionogenic salt linkages present on the surface undergoing more or less complete dissociation in solution. The charge on a particle which results in its motion in an electrical field being the result of the dissociation of certain of these groups, maximum charge is attained when all the surface groups are ionised.

The consequences are that all substances exhibiting electrokinetic phenomena must be ionogenic and that the maximum/

maximum charge attainable is specific for the particle or surface, being a measure of the ionogenic groups present in the surface. The second theory is that of adsorption and this assumes that at an interface an electrolyte is held adsorbed as ion pairs, one kind of ion being held more firmly by the solid than the other. The ion pair thus constitutes a dipole orientated with respect to the interface. The total number of ion pairs adsorbed can be calculated by Gibb's adsorption equation or by the Lippman equation. Of these adsorbed ion pairs, a certain proportion will tend to be dissociated, since the loosely held ion will tend to escape into the body of the solution, leaving the surface with a net charge. The charge and the number of ion pairs dissociating can be determined directly as the zeta potential or indirectly (polarisation). Surface dissociation is brought about by thermal agitation and since electro-static forces are present, the dissociation must be much less than that existing in such an ion pair system when it is dispersed in a three-dimensional phase. The diffuse ionised part of the ion pairs on the surface is the part which causes the electrokinetic phenomena and the whole system of adsorbed ion pairs, together with the diffused portion, constitutes the Helmholtz-Gouy ionic distribution.

The origin of the system of ion pairs can be created in different ways dependent on the nature of the phases in contact with the interface. If one phase is impermeable to ions, the layer is formed by adsorption. This is called specific or Gouy adsorption/

adsorption. If one phase is a conductor and is thus permeable to electrons, the ion pair system is formed by the passage of a current across the interface. A third possibility occurs when one of the phases is ionogenic to give ions which are soluble in the other phase, i.e., when the boundary is selectively permeable to an ion. Here there are two distinct mechanisms, depending on whether the anion or cation passes through the interface. Both cases have been defined as potential determining adsorption.

It must thus be concluded that in general both specific and potential determining adsorption can play a part in the formation of an interphasic layer of ion pairs. Investigation of the layer of ion pairs has been made, for instance, by evaluating the density of population and the extent of surface ionisation. The latter may be done where the extent of dissociation is small by making use of the solubility product of the ion pair system as the criterion. Where acid-base exchange phenomena occur, the ionic concentration may be governed by a Donnan distribution, the Stern-Debye-Hückel treatment of the diffuse part of the ion pair interphase leads to the correct expressions for the variation of mobility as a function of ionic strength and of particle size, within certain ranges of ionic strength. At high electrolyte concentrations, when the diffuse layer thickness is relatively small/

small, mobility experiments have suggested that surface ionisation is reduced, while with solutions of very low ionic strength, the intrusion of a Donnan effect modifies the extent of ionisation.

Many papers on the theoretical and practical aspects of the electrical double layer are included in a symposium published in the Transactions of the Faraday Society. (53). A mathematical treatment of the various electrokinetic phenomena is given by Booth, (54) in which he throws considerable doubt on much of the existing theory and suggests that a great deal of investigation is required, especially with regard to the limiting nature of assumptions made.

Note: This survey is culled largely from publications by Briggs, (15) Horwitz (35) and Rideal. (52).

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HISTORICAL SURVEY OF PRACTICAL APPLICATIONS OF ELECTROKINETIC PHENOMENA.

The main applications of electrokinetics have been found in the reduction of ash, purification, separation and fractionation, dehydration, impregnation, extraction, and application of coatings, using many and varied materials.

Clay, Kaolin and Ceramics.

Clay was purified by Gesellschaft für Elektro-osmose (55, 56), and by Ormandy (57, 58), who also described a dewatering process, his results being criticised by Hopkins (59). Electrophoretic deposition for the dewatering of clays was also described by Speil (60) and by Speil and Thompson (61). Kaolin was purified by methods detailed by Highfield and Ormandy (62), and by Schertel (63), dewatering being carried out by Wilson and Wilcox (64), and by Ralston and Hoseh (65).

Chamberlain (66) described an application of electrophoresis in the extrusion of chemical stoneware and a review of the application of both electrophoresis and electro-osmosis in the ceramics industry was given by Curtis (67). Sokolov (68) electrodialysed clay to remove metallic ions, while Mukherjee, Sen Gupta and Indra (69) experimented with H-bentonites.

A general review of electrophoresis as applied to clays was given by Howat (70).

Gelatin, Glue etc.

Processes and methods for the purification and

fractionation/

fractionation of glue, gelatin and related substances were described by Gesellschaft für Elektro-osmose (71, 72, 73); Elektro-osmose Akt. Ges. (74, 75, 76); Schwerin (77, 78) and Ruppel and Wolf (79). Demineralisation of gelatin was carried out by Oka (80) and of glutin by Vozdvizhenskii (81). Glycerol purification was patented by Elektro-osmose Akt. Ges. (82, 83).

Milk, Casein, Whey.

Electro-osmotic dehydration of milk was described by White and Elten (84). Elder, Easton, Pletcher and Peterson (85) reduced the ash content of acid casein.

Milk and whey were electrodialysed by Woljagin and Scheimpflug (86) and milk by Kato (87) for the production of casein low in ash content.

Whey and whey protein were examined by Watson (88) (removal of salts from whey protein), Bakhalov and Klimovskii (89) (removal of protein and salts from whey), and by Wiechers and de Vries (90) and Aten, Wegelin and Wiechers (91) (reduction of ash content of whey).

Proteins, Amino-acids, Enzymes, Sera etc.

A very great deal of work has been done in this field of chemistry. Purification of sera has been described by Dhéré and Gorgolewski (92) and, together with fractionation, patented by Elektro-osmose Akt. Ges. (93).

Fricke, Fischer and Berchers (94) purified enzymes and the/

the purification of colloids generally has been discussed by Dhéré (95) and Pauli (96). Amino-acid separations have been achieved by Cross (97) and, using the more recent methods of paper-electrophoresis, by Wieland and Fischer (98), Biserte (99) and Durrum (100, 101).

The purification, separation and general examination of proteins have been dealt with by Pauli (102), Tiselius (103, 104), whose moving boundary apparatus and technique were a great step forward in the examination of blood sera and similar fluids, Abramson and Moore (105), Gutfreund (106), Longsworth and MacInnes (107) and Cann, Kirkwood, Brown and Plescia (108), who achieved a separation, on a quantitative basis, of globulins.

Moyer (109) has revieed the applications of electrophoresis to the field of protein chemistry.

Rubber, Latex.

The deposition of rubber anodically has been described by Corbin (110) and the separation of latex particles at a cathode by Siemens - Elektro-osmose G.m.b.H. (111).

Reviews of the applications of electrophoresis in the rubber and latex industry have been given by St. Reiner (112), Hauser and Bender (113) and Génin (114), who also included synthetic resins.

Sewage, Effluents, etc.

Electrodialytic treatments of sewage for the removal of/

of electrolytes, reduction of suspended solids, stabilisation etc. have been reported by Murray (115), Roberts (116), Slagle and Roberts (117) and Beaudoin (118).

The treatment of textile works effluents was described by Magoffin (119) and of distillery slop by Bonacci and Rudolfs (120).

The recovery of potassium oxide from cane molasses distillery slop was achieved by Uchida and Chin (121).

Soil.

Dehydration of turf was described by Schwerin (122).

Studies of the electrodialytic removal of cations from soils have been made by Mattson (123), Wilson (124), Oosugi and Aoki (125), Puri and Anand (126), and Puri and Hoon (127, 128).

The electrophoresis of colloidal soil material was examined by Kovda (129) and Reifenberg (130).

The migration of anions and cations during the electrodialysis of peat was investigated by Wilson and Straker (131, 132).

Consolidation of soil foundations was achieved by Casagrande (133) and hardening of soils in the same way was described by Erlenbach (134).

Surface Coatings.

The electrophoretic deposition of inorganic powders, generally carbonates, from suspension, in most cases in organic liquids/

liquids, has been described by Harsanyi (135), Hansgirg (136), Egyesült Izzolampa és Villamossagi R.T. (137), Philips Patentverwaltung G.m.b.H. (138), N.V. Philips Gloeilampenfabrieken (139, 140), Patai and Tomaschek (141), de Boer, Hamaker and Verwey (142), Lyons (143), Hamaker and Verwey (144), Benjamin and Osborn (145), Hamaker (146, 147), Bidgood and Kent (148), Hill, Lovering and Rees (149) and Biguenet and Mano (150), the main application being the formation of an insulating coating on electrical components.

Carbon was deposited by N.V. Philips Gloëilampenfabrieken (151) and by Frank, Patai and Tomaschek (152), while the deposition of oleo-resinous lacquers was described by Sumner (153).

A review of electrodeposition was given by Roehl (154).

<u>Tanning, Impregnation</u>.

Descriptions of electro-osmotic and electrodialytic processes for tanning have been given by Grasser (155), Electro-osmose Akt.Ges. (156, 157) and Bocca (158).

General impregnation processes were described by Elektro-osmose Akt.Ges. (159, 160) and by Gesellschaft für Elektro-osmose (161, 162).

<u>Water</u>.

The production of water of equivalent purity to distilled water by electrodialytic removal of electrolytes etc. has been described by Illig (163), Patin (164), Dietzel and Müller (165)

Hoffman/

Hoffman and Gortner (166), Jaekel (167), Dietzel (168) and Zhukov, Grigorov and Kozmina (169).

Miscellaneous.

Various other applications have been found for electrokinetic processes.

Elektro-osmose Akt.Ges. (170) described the purification of saccharine juice.

Humic acid of very low ash content has been obtained using electrodialysis by Biesalski and Berger (171).

The electrodialysis of wort and beer has been described by Windisch, Kolbach and Borges (172) and of wine by Paronetto (173).

Gortner and Hoffman (174) purified pulp and Kargin and Vinetskaya (175) cellulose and some of its derivatives, as did Kantor. (176).

The removal of moisture from wood was attempted electro-osmotically by Vlasov and Krylov (177).

Purification of a precipitate of nickel hydroxide was described by Oka (178) and a process of "electro-washing" by Komagata (179).

Fractionation of starch was achieved by Dahl (180).

Hla (181) examined the effect of electrodialysis on a series of minerals and the production of granular alumina was described by Elektro-osmose Akt.Ges. (182, 183).

Collins/

Collins and Grimmett (184) electrodialysed potassium from plant extracts.

An electro-osmotic extraction process was patented by Elektro-osmose Akt.Ges. (185).

The recovery of finely divided magnesium metal from organic liquids was described by Fischer and Peck (186).

Applications to seaweed in the separation of a number of the chemical constituents were given by Florenskii, Litvinov and Bryantsev (187) and the continuous production of alginic acid by electrodialysis is described by Kolle (188).

Treatment of molasses is detailed by Kameyama and Kato (189) and by Reininghaus (190).

Papers of general interest have been published by Ormandy (191) and by Tiselius (192).

Reviews.

The following authors have published reviews on electrokinetics and their technical applications:
Bary (193), Frydlander (194), Prausnitz (195), Akizawa (196), Duclaux (197), Sarrot du Bellay (198), Illig (199), Chemnitius (200), Kendall and Gebauer-Fuelnegg (201), Schönfeldt (202, 203), Hutton (204), Rao (205), Vigneron (206), Wiedemann (207) and Causse (208).

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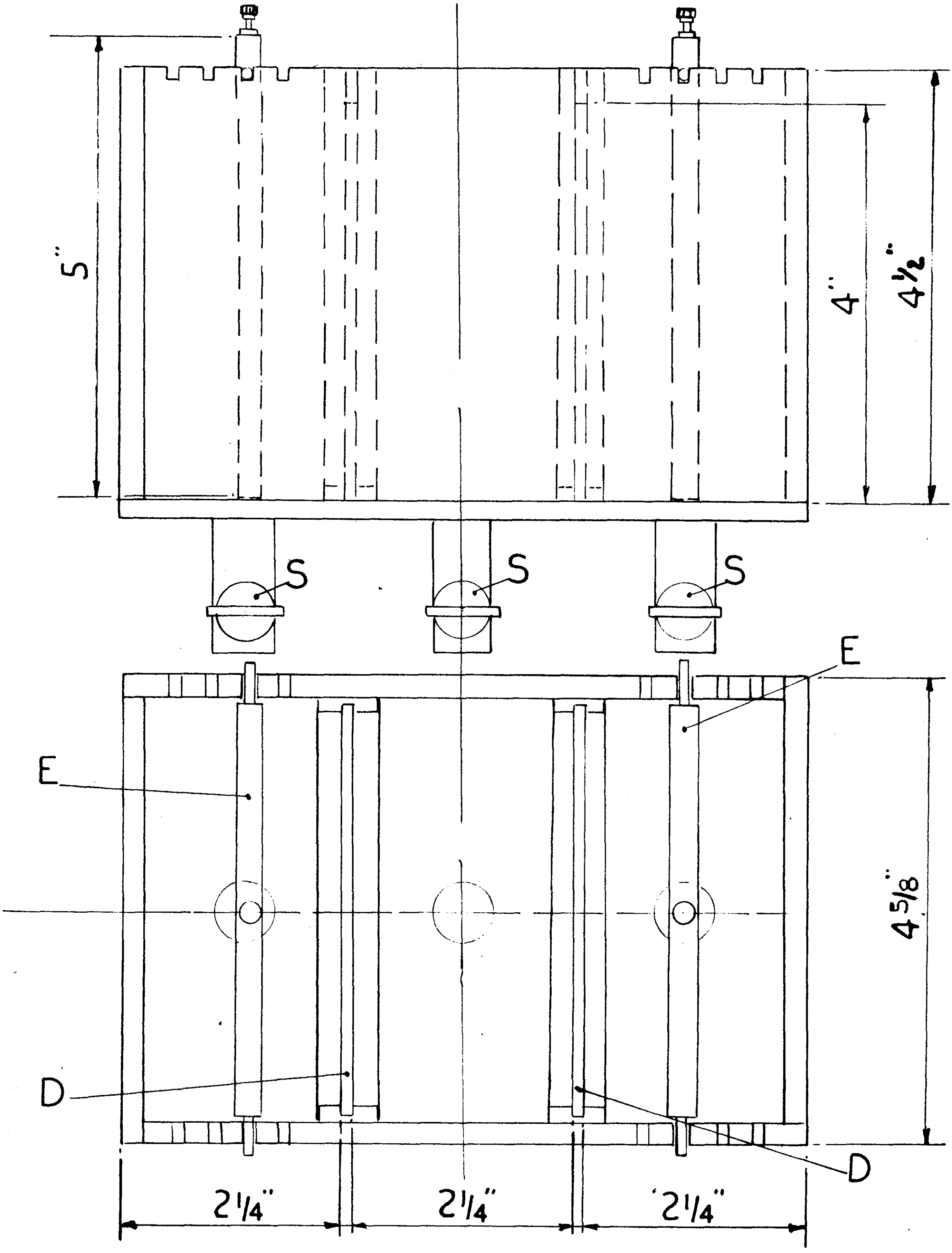
DEVELOPMENT OF APPARATUS.

In this section the various types of apparatus used for electrodialysis and electrodeposition, together with the electrical circuits employed, are described in detail, and various reasons given for the design of each.

Electrodialytic Cell I.

The cell is shown in Figure 1 and takes the form of a rectangular box. It is constructed from $\frac{1}{4}$" Perspex sheet and is $6\frac{1}{2}$" long, $4\frac{1}{8}$" broad and $4\frac{1}{2}$" deep (internal dimensions). The box is divided into three sections, the outer ones 2" and the centre $2\frac{1}{4}$" long, by two porous earthenware diaphragms (D, D), cemented into grooved rubber strips which are, in turn, cemented in position on the sides and bottom of the cell. A circular hole, $\frac{3}{8}$" diameter, is cut in the bottom of each section in a central position, and glass tubes, fitted with stopcocks, (S.S.S.) project downwards from them, a seal being obtained by flaring the end of each tube.

Four equally spaced notches are cut in the top edges at each side of the two outer sections to secure the electrodes. The electrodes (E.E.) are $\frac{1}{4}$" iron or carbon plates, 5" long and 4" broad, a brass terminal being tapped into the top edge of each. The electrodes are provided with projecting brass arms, $\frac{1}{2}$" long, placed $\frac{5}{8}$" from the top. Grade CF4 Aerox diaphragms are used, 4" long, 4" broad and $\frac{1}{8}$" thick. These are ceramic plates with a pore volume of 33.2 per cent. and pore diameter of 7.2 microns. The permeability, expressed as the volume in ml. passed by 100 sq.cm. per hour at 20°C. and at a pressure of 10 cm. of water, is 285 ml. In use, the cell is supported on a metal frame which permits receiving/



ELECTRODIALYTIC CELL.

FIGURE I

receiving vessels to be placed under the outlets from the three sections. A glass paddle stirrer, driven by an electric motor, is provided for the centre section.

During a series of preliminary tests, several difficulties were encountered:

(a) Inefficient stirring of the suspension in the centre compartment.

This was due to the section being rectangular in shape, limiting the size of the stirrer blades to the smaller dimension.

(b) Building up of a hydrostatic head due to electro-osmotic flow, this effect acting against the electrical effect and reducing it.

(c) Leakage of liquid past the edges of the diaphragms.

(d) Non-removable nature of the diaphragm arrangement.

These difficulties can be overcome as follows:

(a) Centre section square in shape.

(b) Provision of overflow outlets in the front face of each section.

(c) and (d) Diaphragms held between rubber gasketed flanges, the cell being made in three sections, held together as a unit by screws at these flanges.

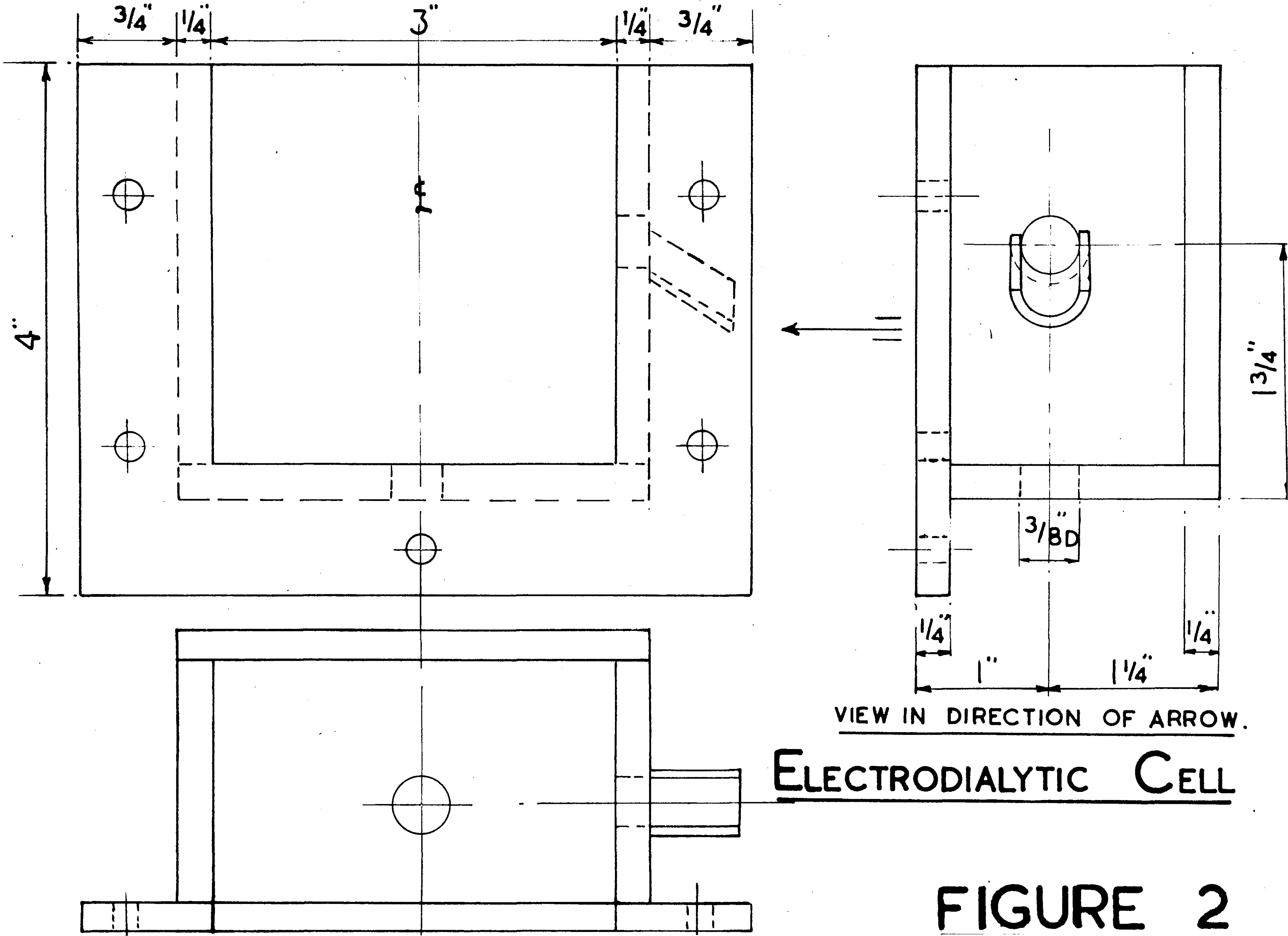
Electrodialytic Cell II.

This cell is shown in Figures 2 and 3 and in Plates 1 and 2, and incorporates the modifications described above. The cell is again in the form of a rectangular box. It is constructed from ¼" Perspex sheet and is, when assembled, 7" long, 3" broad and 3" deep (internal dimensions). It is made in three sections, outer left, centre and outer right, the last named being a mirror image of the first.

The outer sections (Figure 2) consist of a base and three sides and are 2" long, 3" broad and 3" deep (internal dimensions). A circular hole ⅜" diameter is cut in the centre of the base and is provided with a rubber bung, fitting flush with the inside surface of the cell. This hole serves for complete drainage of the compartment. A similar hole is cut in the centre of the front face and from this projects a sloping semi-circular trough, the overflow outlet. The sections have a flange, 1" wide, on the inner edge and a rubber gasket is provided for it.

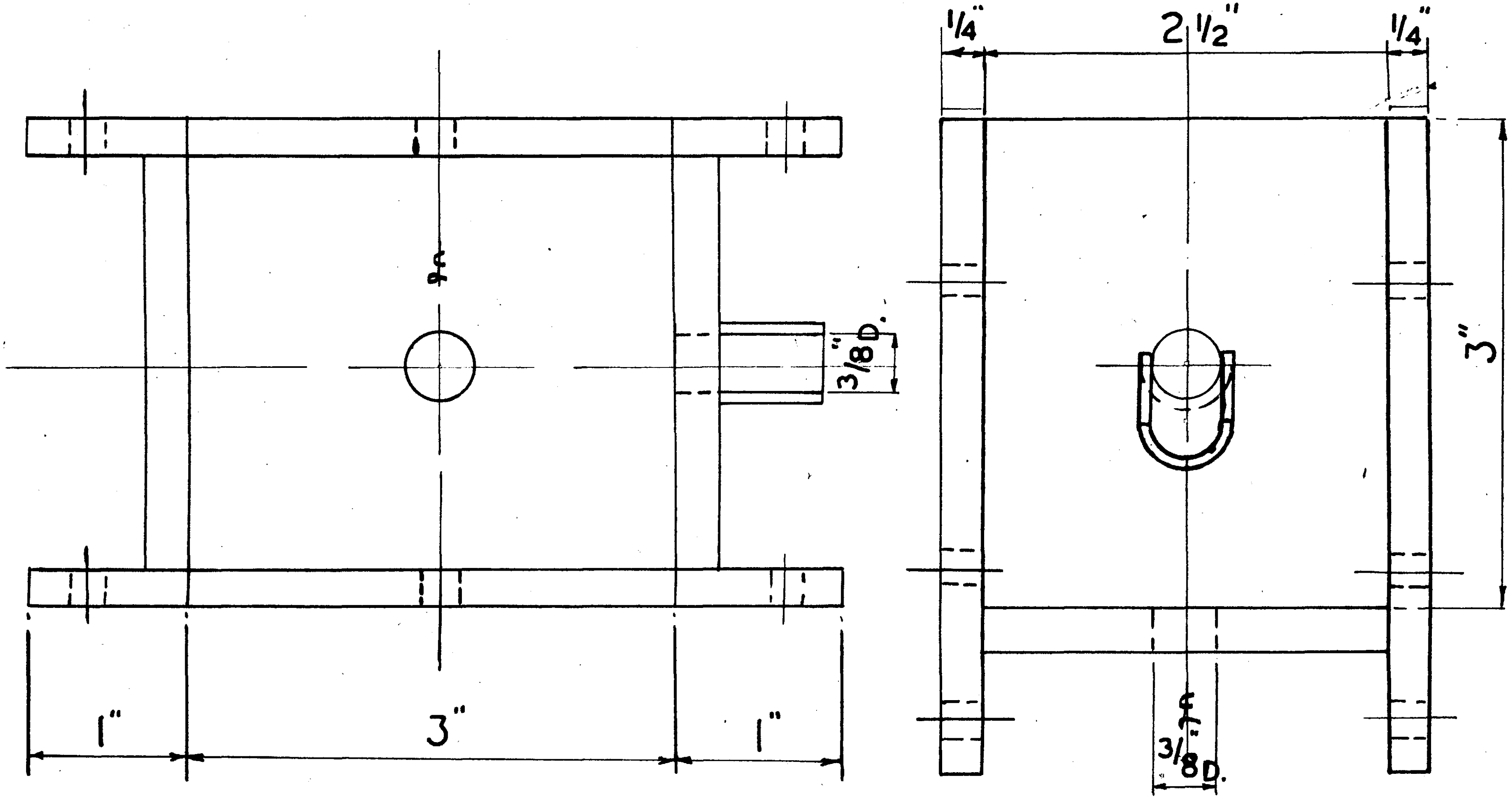
The centre section (Figure 3) has a base and two sides, being 3" long, 3" broad and 3" deep (internal dimensions). Both edges have a flange, 1" wide, fitted with a rubber gasket. The section is, otherwise, the same as the outer sections, having holes cut in the centre of the base and of the front face, the latter leading to an outlet trough.

The/



ELECTRODIALYTIC CELL

FIGURE 2



PLAN

FRONT ELEV.

ELECTRODIALYTIC CELL

FIGURE 3

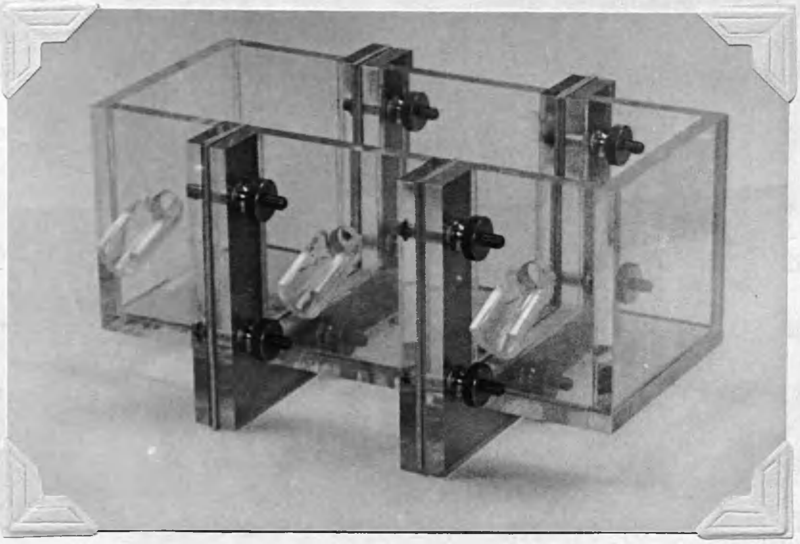


Plate 1.

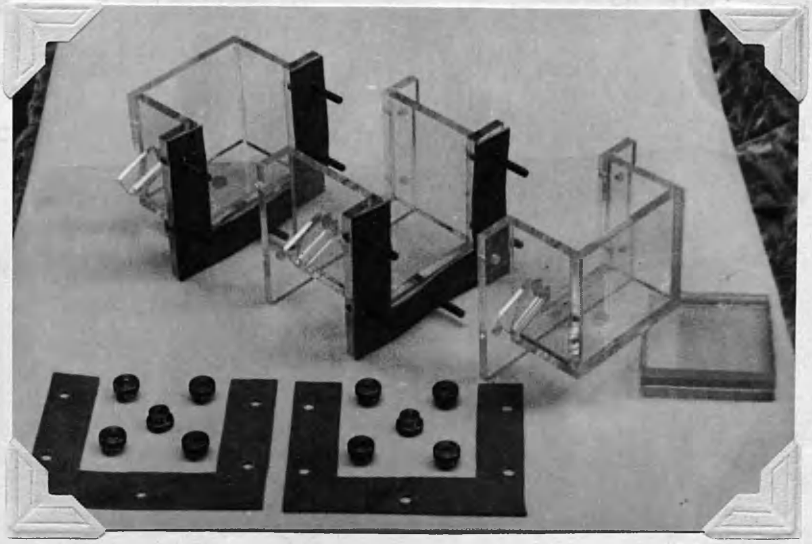


Plate 2.

The three sections are joined together by means of brass screws, cemented into the left hand flange at each joint, these screws passing through the rubber gaskets and through holes provided in the right hand flange. Tightening of the flanged joints is effected by knurled brass heads, which are screwed hard against the right hand flange at each joint. There are five screws to each joint, two at each side and one placed centrally in the bottom edge.

The electrodes used are made of $\frac{1}{4}$" carbon sheet, being $2\frac{3}{4}$" broad and 3" long. Brass terminals are tapped into the top edges. The electrodes are attached to the cell by means of L-shaped brass clips, which fit tightly over the top edge of the cell walls.

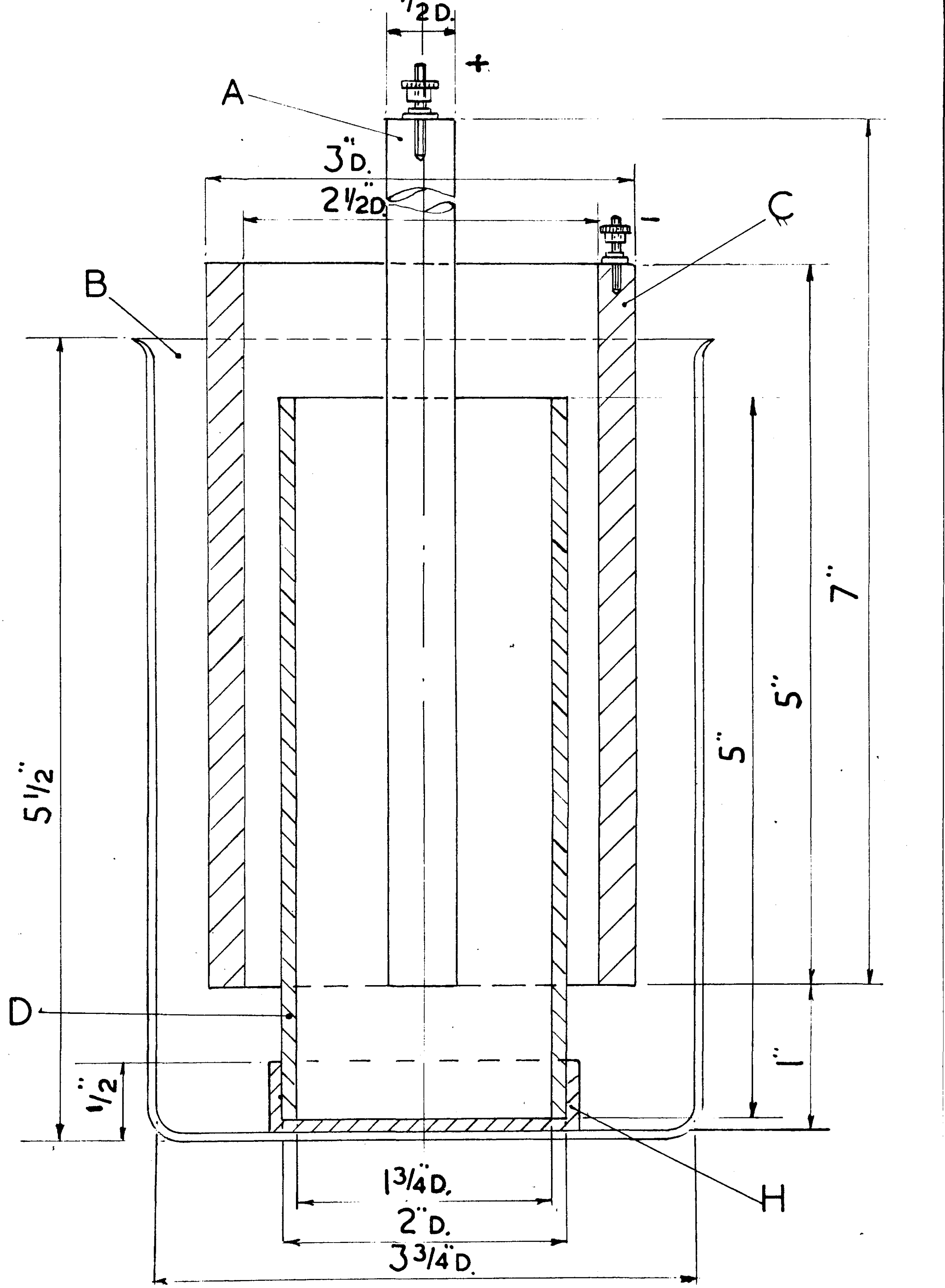
The diaphragms used can be of practically any material, the effective dimensions being 3" breadth and 3" length. Among the diaphragms which have been used are Aerox CF4 earthenware, filter cloth, cellophane, parchment paper and cellulose acetate.

This cell has proved satisfactory over a very large number of tests.

Electrodialytic Cell III.

The cell is shown in Figure 4 and is circular in form. The outer vessel is a glass beaker (B). The diaphragm (D) is a porous earthenware pot, 5" long and $1\frac{3}{4}$" internal diameter. The anode (A) is a carbon rod, 7" long and $\frac{1}{2}$" diameter, while the cathode (C) is a carbon cylinder, 5" long and $2\frac{1}{2}$" internal diameter. The diaphragm, which is Aerox grade CF4, rests in a small bakelite holder (H), cemented on to the centre of the base of the beaker. The various parts are set up concentrically, the anode rod at the centre, with the diaphragm between it and the cathode cylinder, the assembly being held rigidly by clamps in a central position in the beaker.

This cell was designed as a prototype for Cell V, to find the effect of a concentric arrangement of electrodes and diaphragm.



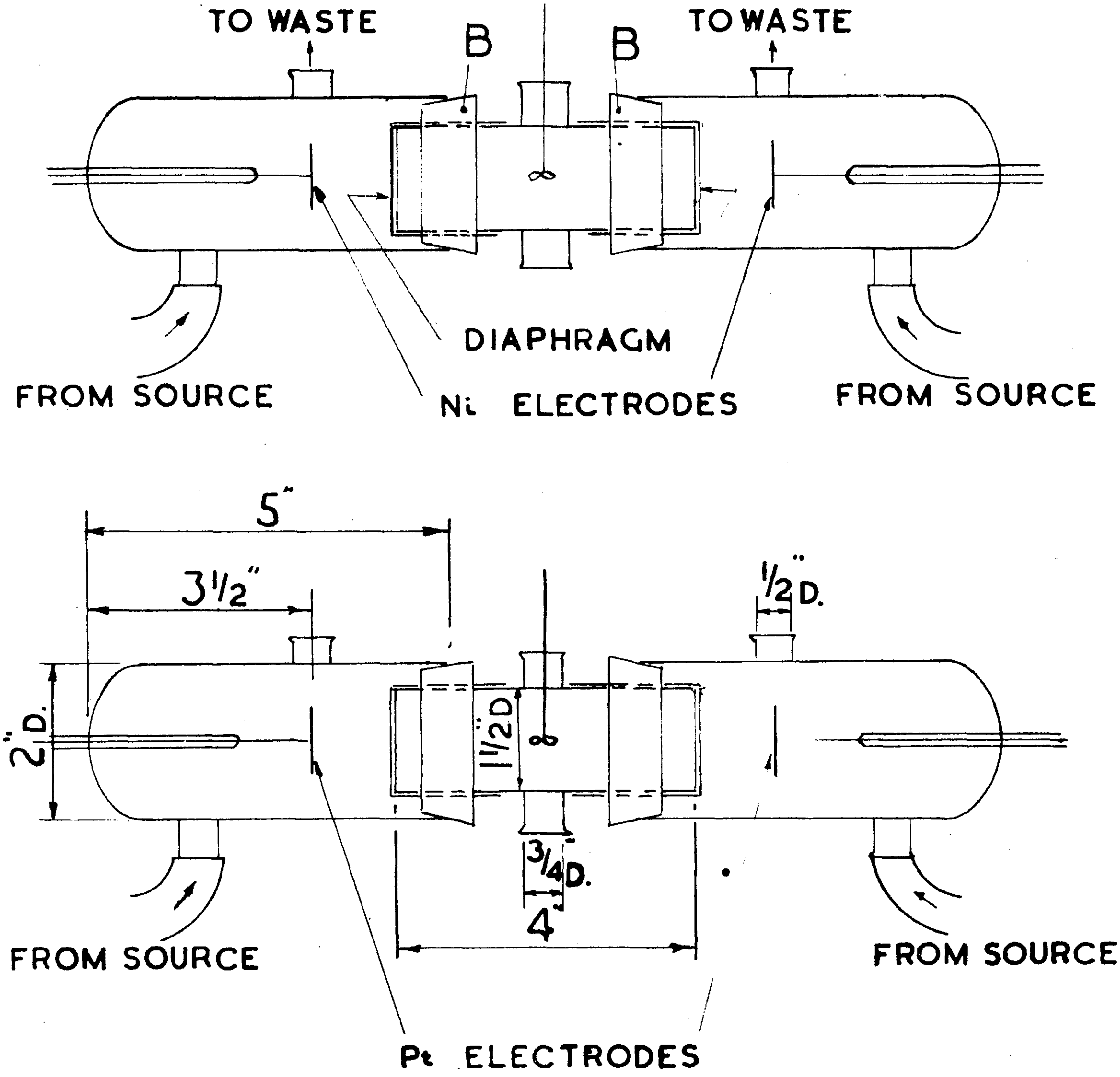
ELECTRODIALYTIC CELL

FIGURE 4

Electrodialytic Cell IV.

The cell is shown in Figure 5 and in Plate 3. It is constructed from glass, and is again in three separate sections, outer left, centre and outer right. The outer sections are mirror images of one another, and consist of a glass tube, 5" long and 2" diameter, closed at one end. Two sets of outer sections are available. One pair have nickel electrodes in a glass support, sealed into the tube through the closed end, the electrode face being circular in shape and having holes cut in it to facilitate the escape of gas formed by electrolysis. Inlet and outlet holes are provided in the top and bottom of the tube to allow circulation of liquid through the compartment. The other pair of outer sections are similar to the first but are equipped with platinum electrodes, the electrode faces being square in shape. Inlet and outlet holes are again cut in the top and bottom of the tube.

The centre section consists of a glass tube, 4" long by 1½" diameter, holes being cut in the top and bottom for filling and emptying the compartment. The top aperture also accommodates a small paddle stirrer for agitation of the suspension in the section. Rubber bungs (B.B.) are bored to fit tightly on to the centre section and serve to hold the diaphragms in place, the outer sections fitting closely on to the outer edge, giving a water-tight join between the sections/



ELECTRODIALYTIC CELLS

FIGURE 5

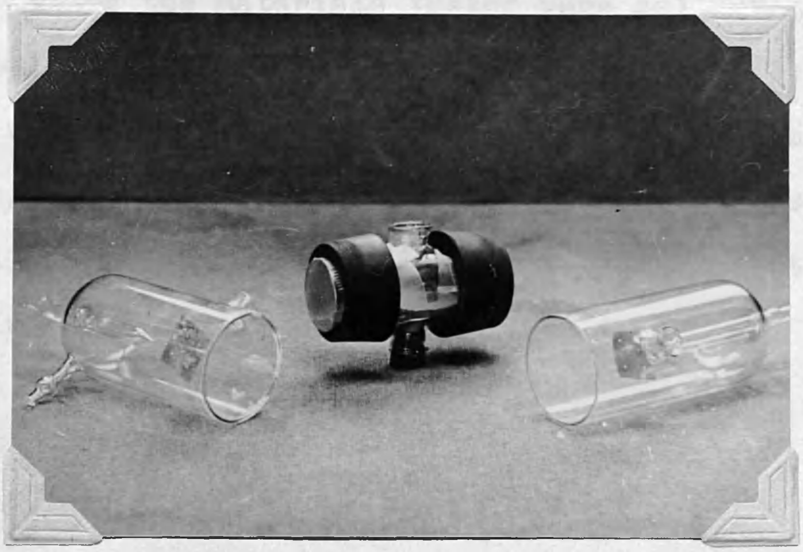


Plate 3.

sections. The nickel electrodes are joined to a piece of tungsten wire by silver solder, the tungsten wire providing the connection to the mains leads. The platinum electrodes are fused to platinum wire.

The diaphragms which can be used with this cell are numerous. Among the materials tested were cellophane, parchment paper, cellulose acetate and regenerated cellulose. This cell was designed to permit tests with cellulosic diaphragms, the diaphragms and the materials of construction of the cell (glass, rubber and platinum) giving little chance of contamination.

Electrodialytic Cell V.

The cell is shown in Figure 6 and Plate 4, and is cylindrical in form. The outstanding feature of this cell is that it provides for continuous circulation of both the anode and cathode liquids.

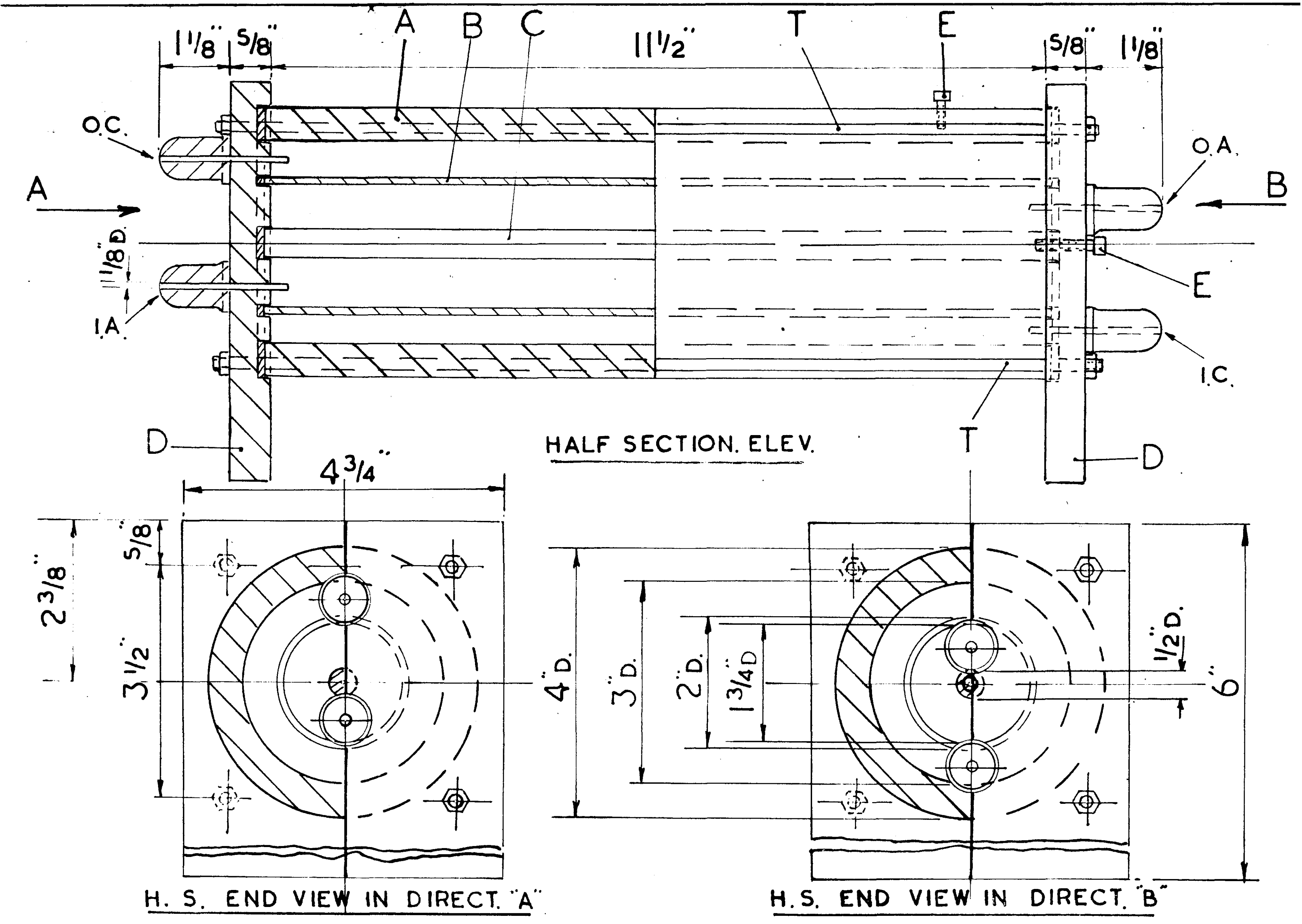
The anode (C) is a carbon rod, $\frac{1}{2}$" diameter and $11\frac{3}{4}$" long. The diaphragm (B) is a porous earthenware tube $1\frac{3}{4}$" internal diameter, $11\frac{3}{4}$" long and $\frac{1}{8}$" wall thickness. The cathode (A) is a carbon cylinder, 3" internal diameter and $11\frac{3}{4}$" long by $\frac{1}{2}$" wall thickness.

These three parts are held in position by means of end plates (D. D.) $4\frac{3}{4}$" by 6" by $\frac{5}{8}$" made of Tufnol. The end plates are grooved on the inner face to allow each of the parts to be positioned. Rubber gaskets are provided to give watertight joints. The entire assembly is held tightly together by four brass tie rods (T. T.) passing through the end plates.

Brass nozzles are used as inlets and outlets to and from the anode and cathode compartments (IC = inlet to cathode, OC = outlet from cathode; IA = inlet to anode; OA = outlet from anode). Brass screws (E. E.) tapped into the carbon rod and cylinder are used as the electrical terminals.

Reservoirs Two 1 litre beakers are used as reservoirs for the anode and cathode liquids, each being provided with an inlet and outlet, the inlet being at the top. These beakers are held in position by felt-lined brass clips (Plate 4).

Circulation is carried out using Stewart Turner centrifugal pumps. (Plate 4.)



HALF SECTION. ELEV.

H. S. END VIEW IN DIRECT. "A"

H.S. END VIEW IN DIRECT. "B"

CIRCULATING ELECTRODIALYTIC CELL. FIGURE. 6

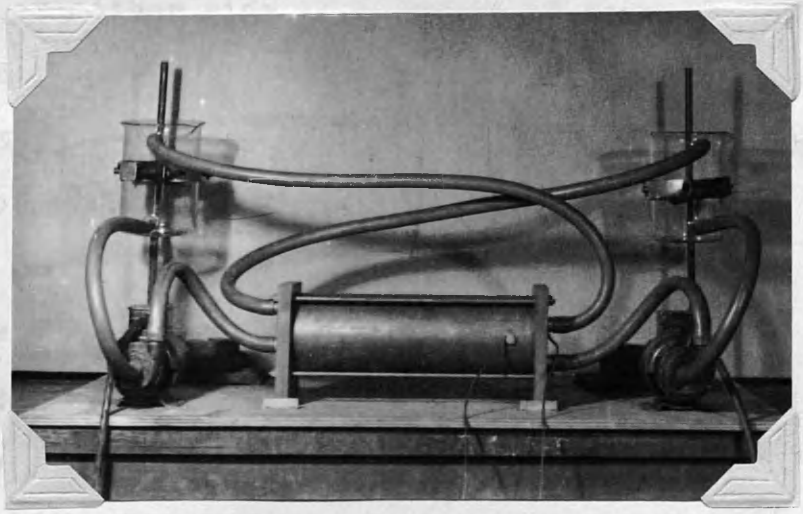


Plate 4.

Electrodeposition Cell I.

This cell is shown in Figure 7 and is made from simple components. The central carbon rod (C), 6" long and $\frac{1}{2}$" diameter, is the cathode. It is encircled by a cylinder of wire gauze (A), 5" long and 1$\frac{1}{2}$" diameter, which serves as the anode. Two rubber rings (R.R.), 2" diameter, having a $\frac{1}{2}$" hole cut in the centre are placed on either side of a square of gauze (G), 5" by 5", having a 1$\frac{1}{2}$" diameter hole cut in its centre, the lower ring insulating it from the anode cylinder. The two rings together serve to position the cathode rod and the square of gauze supports the entire assembly on the edges of the vessel which contains the suspension from which deposition is to be made. The lower rubber ring is wired (W) on to the top of the anode cylinder while the other ring is not attached.

Difficulties which arose during the operation of this apparatus were:

(a) Sagging of the wire gauze support, causing a greater depth of the electrode assembly to be immersed in the suspension.

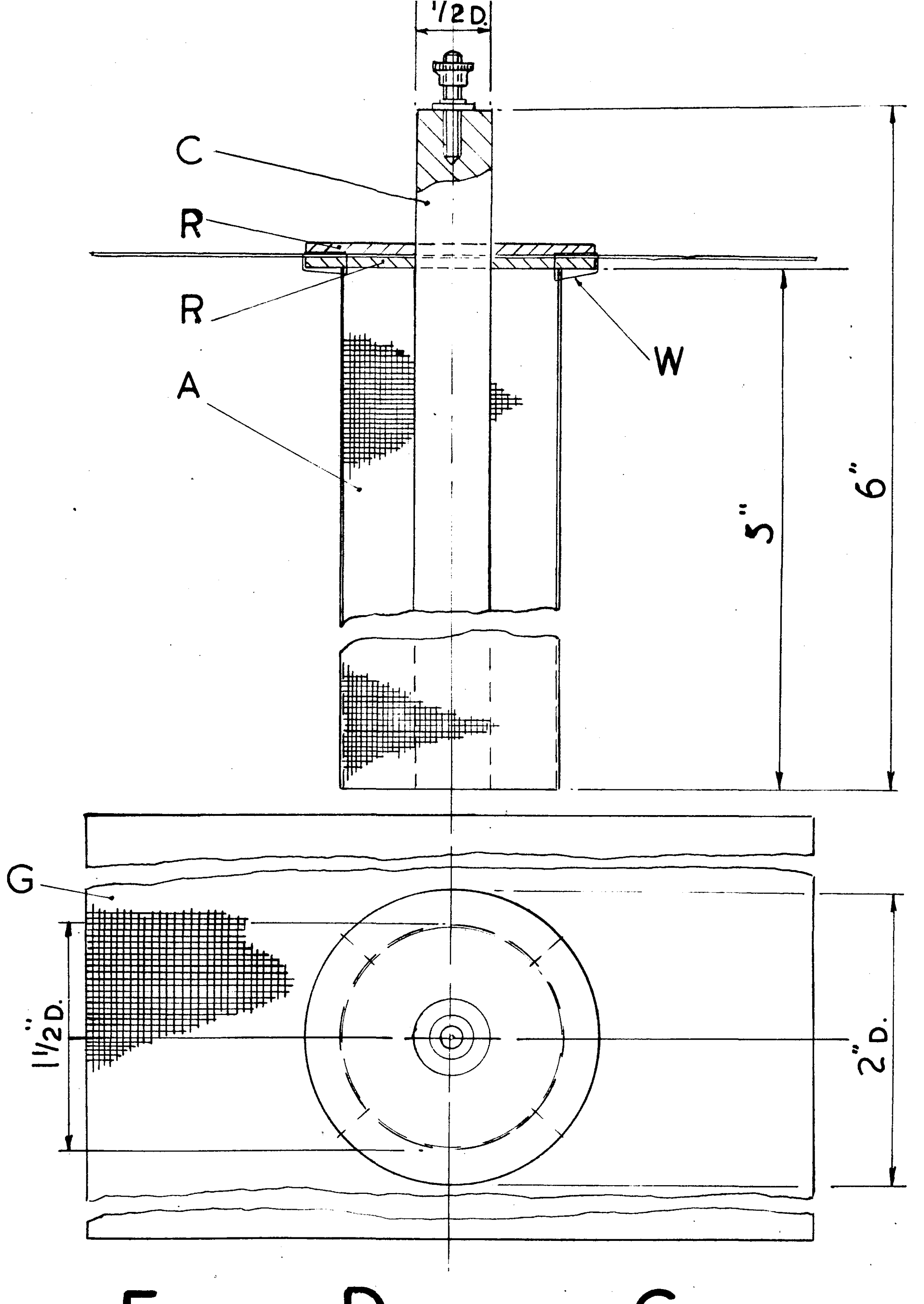
(b) Movement of the cathode relative to the anode, not necessarily during a test but certainly from one test to another.

(c) Rusting of the anode gauze after tests employing water as the suspending medium.

(d) Tendency for cathode rod to slip below the original setting, protruding slightly beyond the end of the anode cylinder.

These difficulties can be rectified in the following manner:

(a)/



ELECTRO DEPOSITION CELL

FIGURE 7

(a) Use of a rigid material for supports. Wood, since it is an insulator, is preferred.

(b) Insertion of positioning rings at the top and some distance down the assembly.

These should also be of insulating material, Sindanyo being suitable.

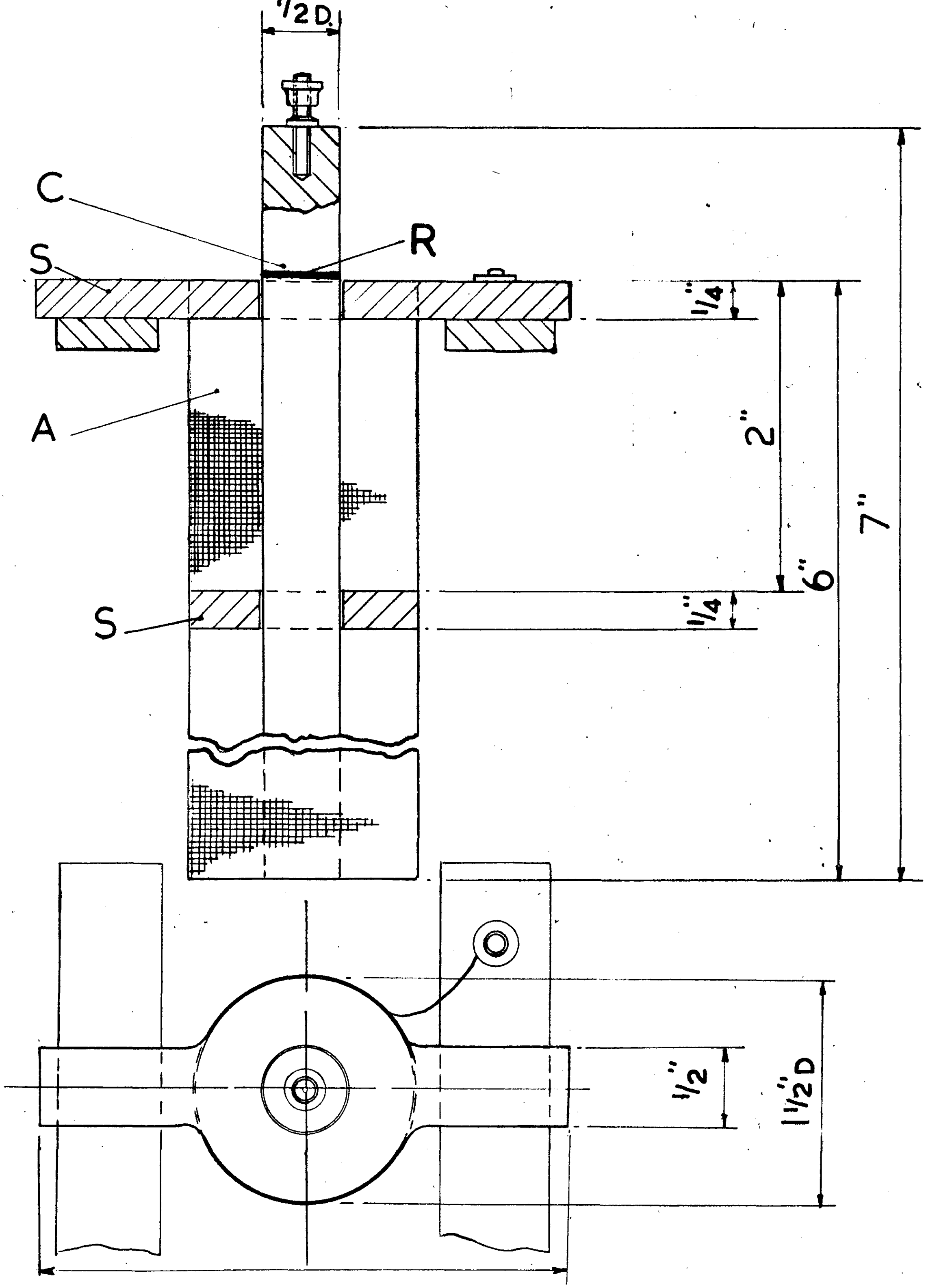
(c) Use of stainless steel gauze for the anode cylinder.

(d) Provision of an arresting collar of rubber at the top of the assembly.

Electrodeposition Cell II.

This cell is shown in Figure 8 and incorporates the improvements discussed in the previous section. The cathode (C) is a carbon rod, 7" long and ½" diameter, with a brass terminal tapped in to the top. The anode (A) is a cylinder of stainless steel gauze, 6" long and 1½" diameter. The gauze is centre-punched on to two pieces of Sindanyo sheet (S.S.), ¼" thick. The upper piece consists of a circular part, 1½" diameter with two lugs, 1" long and ½" broad at opposite sides. The lower piece is a 1½" diameter circle and is placed 2" from the top of the anode cylinder. Both pieces have a ½" diameter hole cut centrally in them. A wooden strut, 6" long, ¾" broad and ¼" thick, is attached under each lug of the upper Sindanyo ring, these struts serving as supports for the assembly.

The cathode rod is a tight fit through the holes in the Sindanyo rings, which serve to centralise it with respect to the anode and make the relative positions exactly reproducible, since they also keep the anode cylinder in its true shape. A small rubber ring (R), which fits tightly round the cathode rod, rests on the top Sindanyo ring in such a way that the bottom of the cathode rod is always exactly level with the bottom of the anode gauze.



ELECTRO DEPOSITION CELL.

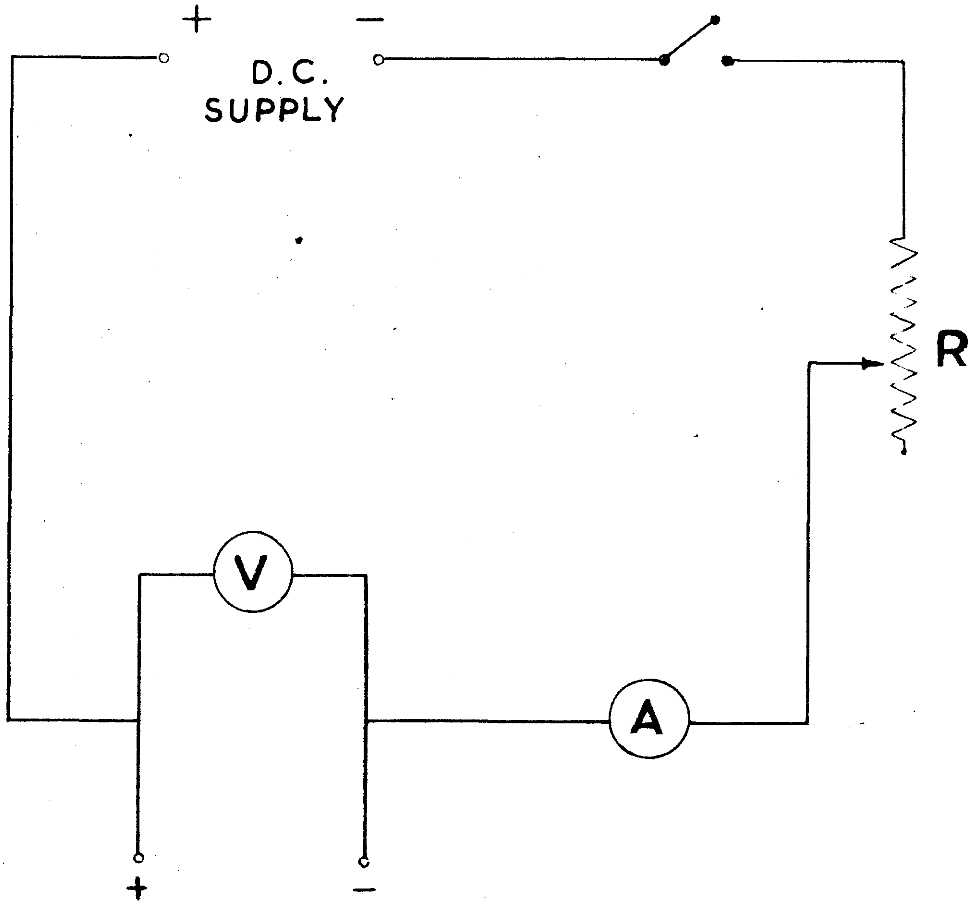
FIGURE 8

ELECTRICAL CIRCUITS.

Electrical Circuit I.

This consists (Figure 9) simply of a variable resistance (R), ammeter and on/off switch in series with the D.C. mains supply. A voltmeter is placed across the output terminals.

The circuit was found to be unsatisfactory in that the variable resistance did not give adequate control of the potential applied across the output terminals. The ammeter was not sufficiently accurate at lower current values.



ELECTRICAL CIRCUIT FOR ELECTRO OSMOSIS

FIGURE 9

Electrical Circuit II.

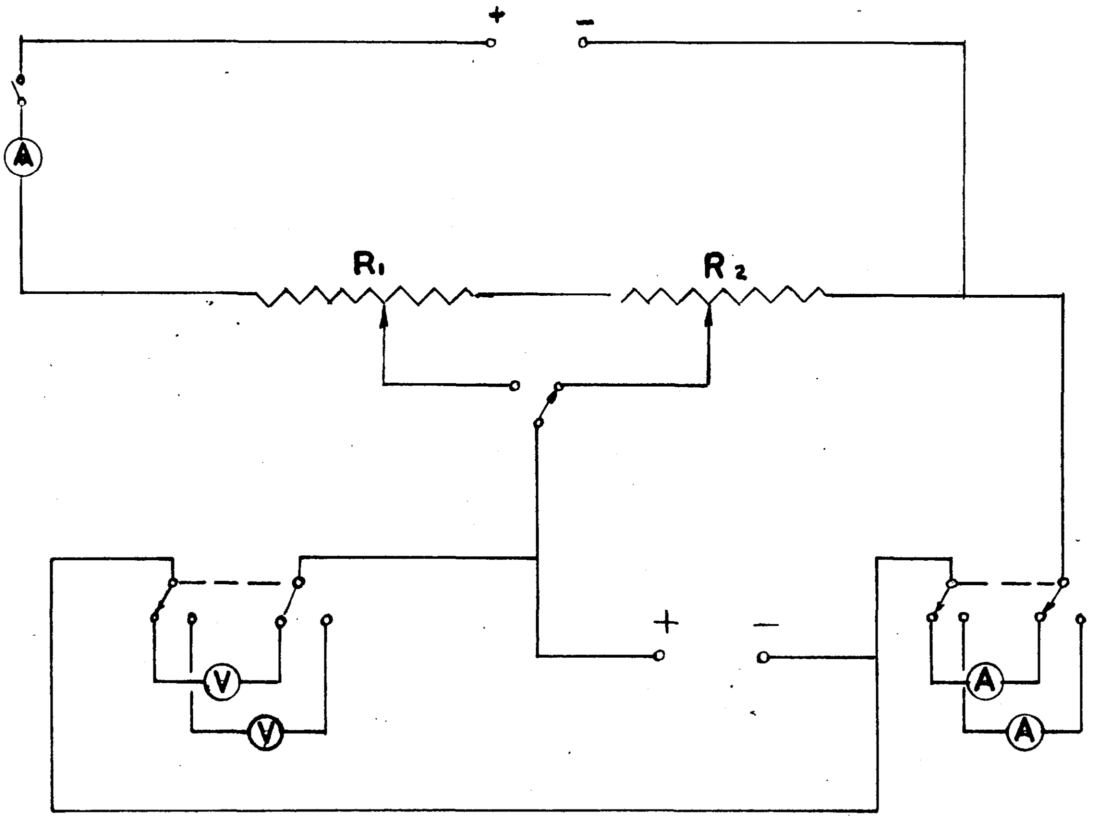
In this improved circuit (Figure 10), the potential applied across the output terminals was varied by a potential dividing system. Two variable resistances, R_1 and R_2 were connected in series between the input terminals. Connection to the output circuit was made from either R_1 or R_2 using a double throw switch.

An on/off switch was inserted in the input circuit as was an ammeter to measure the current in the shunted sections of the resistance.

The current flowing between the output terminals was measured on either of two ammeters (0-0.5 or 0 - 5 amps.) depending on the range required, a double-pole, double-throw switch being used.

The applied potential across the output terminals was measured on either of two voltmeters (0-40 or 0-250 v.) as required, a double-pole, double-throw switch again being employed.

This arrangement gave close control of applied potential and allowed accurate readings both of voltage and current to be made.



ELECTRICAL CIRCUIT FOR ELECTRO-OSMOSIS

FIGURE 10

EXPERIMENTAL SECTION.

PART I - INORGANIC

A. ELECTRODIALYSIS.

General.

Electrodialysis is employed to effect separations, mainly of organic materials from each other and from inorganic contaminants. Little work has, however, been done on the separation of inorganic materials from one another.

The work in this section is concerned with the investigation of the possibilities of separating calcium and magnesium as they occur in dolomite, the natural double carbonate.

Dolomite.

This mineral is found in very large deposits in most of the industrial countries of the world. It is, as has already been stated, the double carbonate of calcium and magnesium, $Ca.Mg.(CO_3)_2$, and provides a rich source of magnesium.

Existing Processes for the Separation of Magnesium from Dolomite.

Various chemical processes have been devised for the production of magnesium from dolomite and the main ones are summarised below:

(1) A German method is to crush the ore and calcine it at about 1200°C., giving a magnesia-lime mixture which is then leached with potash plant end-liquors, composed mainly of magnesium chloride. The insoluble magnesia is filtered off, dried and chlorinated in a special furnace.

Alternatively, the calcium chloride filtrate is treated with ammonium carbonate which precipitates calcium carbonate, leaving ammonium chloride in solution. The filtrate is now stirred/

stirred with magnesium hydroxide from the first filtration forming magnesium chloride and ammonium hydroxide. The suspension is heated to 100°C. when the ammonia is driven off and can be carbonated to give a further supply of ammonium carbonate, the magnesium chloride being returned to leach a further charge of magnesia-lime from the kiln.

(2) The Chesny process involves the treatment of dolomite with sea-water, all of the magnesium in the brine and in the dolomite being recovered as crystalline magnesium hydroxide, which can be readily calcined.

The ore is crushed and calcined at 1350-1375°C. It is further crushed and slaked with freshly softened water. The slurry then passes to a reactor tank into which sea-water is introduced in such a way as to cause a tangential swirl to develop. The thick sediment of magnesium hydroxide is separated and vacuum filtered at 90°C., at which temperature the hydroxide is quite insoluble. The hydroxide is now ready for calcining. The sea-water is pre-treated with a small amount of dolomite slurry from the slaker tank to precipitate any soluble bicarbonates present.

(3) The Mitchell process for the production of magnesia from dolomite is based on the fact that magnesium carbonate decomposes at about 800-850°C., whereas calcium carbonate is stable to 900°C.

The ore is crushed and calcined at the lower temperature, being subsequently passed through a series of settling tanks in which/

which the magnesium oxide, being lighter, passes over while the calcium carbonate settles.

(4) An Italian process involves the treatment of ground dolomite with carbon dioxide at a pressure of 150 lb./sq.in. to produce soluble magnesium bicarbonate, which is then separated by filtration. It is converted to the chloride by the addition of hydrochloric acid and the process completed by electrolysis of the aqueous solution.

(5) Flotation methods have been tried in the United States with success.

(6) The Pattinson process involves calcination, slaking and the formation of a slurry through which carbon dioxide is blown, forming calcium carbonate (insoluble) and basic magnesium carbonate in solution. The weak solution of the basic magnesium carbonate is heated to drive off carbon dioxide, which is re-circulated. The slurry of magnesium hydroxide is thickened, vacuum filtered and dried.

PREPARATION OF MATERIALS.

Dolomite.

A sample of the mineral was obtained from Duror, Argyllshire. The sample was broken down with an iron pestle to give 1"-2" lumps and these passed through a jaw-crusher. The resultant material was further reduced in size by passing it through a roller-crusher. Final grinding was done in a pebble-mill. The fraction of dolomite passing 200 mesh B.S.S. but retained on 300 mesh B.S.S. was collected.

Half-calcined dolomite.

A sample of Duror dolomite was prepared as described above, the fraction taken being the material passing a 300 mesh B.S.S. sieve.

Figure 11 shows the differential thermal analysis curve for Duror dolomite. Two major endothermic reactions take place, the first, at 810-840°C., being the conversion of magnesium carbonate to the oxide and the second, at 840-920°C., being the similar conversion of calcium carbonate.

It is thus possible by calcining the mineral at a temperature of 825-835°C., to obtain a material consisting mainly of magnesium oxide and calcium carbonate.

A sample of half-calcined Duror dolomite was prepared in this manner, roasting a charge of the mineral in an electric furnace at a temperature of 825-835°C. for one hour. It was noted that, after calcination, the colour of the mineral had changed from almost white to a quite definite brown, presumably due to the oxidation of ferrous to ferric iron, present as an impurity. Microscopic examination showed the formation of an amorphous powder, the dolomite being wholly crystalline before treatment.

Pure chemicals.

Samples of pure calcium and magnesium carbonate and of magnesium hydroxide were prepared, the calcium carbonate and magnesium oxide being of Analar standard.

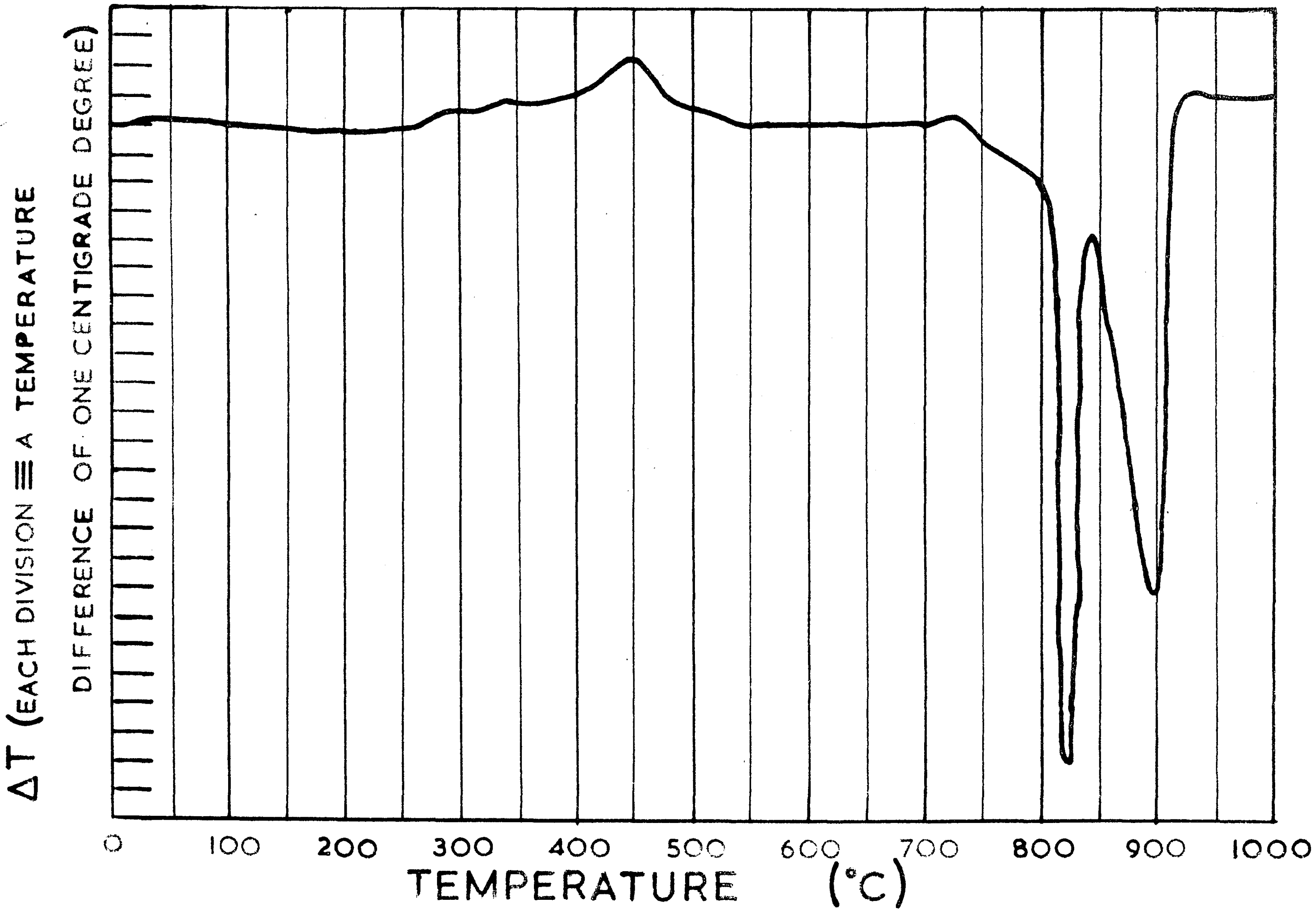

ΔT (EACH DIVISION ≡ A TEMPERATURE
DIFFERENCE OF ONE CENTIGRADE DEGREE)
0
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE (°C)

FIGURE 11

It should be noted that artificially prepared magnesium carbonate is not a pure carbonate but is basic in character, approximating to the formula $3\ Mg.CO_3.Mg(OH)_2.4H_2O$ in the "heavy" grade which was used.

ANALYSIS OF MATERIALS.

Analar calcium carbonate.

The Analar specification was taken.

Analar magnesium oxide.

The Analar specification was taken.

"Heavy" magnesium carbonate.

The magnesium content was determined gravimetrically by precipitation with 8-hydroxyquinoline ("oxine") following the method described by Vogel (209).

Dolomite.

Analysis was made using the method given by Vogel (210).

Acid-insoluble material was determined by dissolving a sample in hydrochloric acid and evaporating to dryness, dissolving the residue in a mixture of concentrated hydrochloric and nitric acids and again evaporating to dryness. The residue was moistened with concentrated hydrochloric acid to dissolve basic salts and then digested with warm water, filtered washed, and ignited to constant weight in a silica crucible.

R_2O_3, the oxides of iron, aluminium, manganese etc., were estimated by precipitation with ammonium hydroxide, the precipitate/

precipitate being filtered, washed, and ignited to constant weight in a silica crucible.

Calcium oxide was determined by precipitation with ammonium oxalate, the precipitate being filtered, washed, dissolved in sulphuric acid and the oxalate ion estimated volumetrically using potassium permanganate.

Magnesium oxide was determined gravimetrically by precipitation with 8-hydroxyquinoline, the precipitate being filtered on a sintered glass crucible (1G3), washed, dried at 105°C., and weighed as $Mg(C_9H_6ON)_2 \cdot 2H_2O$.

The analytical results are shown in Tables I and II.

TABLE I.

Analysis of Pure Chemicals.

Chemical	Ca(%)	Mg(%)
Calcium carbonate (Analar)	40	-
Magnesium oxide (Analar)	-	60
Magnesium carbonate (Heavy)	-	25.6

TABLE II.

Analysis of Duror Dolomite.

Material	Percentage			
	Acid Insoluble	R_2O_3	CaO	MgO
ex 200 on 300 mesh B.S.S.	4.22	0.79	29.35	20.61
Original	12.45	0.79	27.26	19.14
Half-calcined ex 300 mesh B.S.S.	5.44	0.91	38.43	28.12

PRELIMINARY TESTS.

A number of preliminary tests were made using Electrodialytic Cell I (Figure 1), the electrical circuit employed being that shown in Figure 9.

Samples of Duror dolomite were suspended in distilled water, with or without the addition of acid. These tests were of a qualitative nature, designed to discover the faults of the apparatus and to give some indication of the extent of migration of material to the outer sections.

Test 1.

A suspension of 5.00 g. of dolomite in distilled water was used in the centre compartment, the outer sections containing distilled water. Electro-osmotic flow of water into the cathode section was observed, an increase of level of 5.1 cm. being obtained in 40 minutes, representing a flow of about 250 ml. of water. Contamination of the suspension in the centre compartment was caused by iron dissolving from the anode. The electro-osmotic flow was seen to be decreasing during the test and it was found that if the levels in the anode and centre compartments were brought up to the same height as that of the cathode compartment, the flow remained steady - there being no hydrostatic head to be overcome. The value of pH in each section was determined approximately at the end of the test when it was found that the anode chamber pH was 5.0, that of the centre chamber 5.2 and that of the cathode chamber 8.0.

Very little discoloration due to iron was seen in the cathode liquid, probably owing to the iron being completely precipitated on reaching the diaphragm, because of the change in pH at that point. The cathode compartment liquid was evaporated to dryness and only a trace of solid was left.

Test 2.

In this test 10 ml. of 0.5N. hydrochloric acid were added to the water in the centre compartment before the charge of 5.00 g. of dolomite was introduced. A carbon electrode was used as anode to prevent contamination of the charge with iron. It was noted that the flow of water was from the cathode section to the centre, a drop in level of the cathode liquid of 1.3 cm. occurring during the test. There was no apparent change of level in the anode compartment. A colloidal precipitate of ferric hydroxide formed in the cathode chamber, none of which migrated from it. Considerable heat was imparted to the water in the cell, the final temperature in the centre section being 34°C. The pH of the three compartments was determined before and after the test, the figures obtained being:-

	Anode.	Centre.	Cathode.
Before	5.0	2.0	5.0
After	2.0	6.0	8.5

Owing to the iron precipitate in the cathode section, it was decided to carry out the test again with the electrodes reversed.

Test 3.

The test was made as above with the anode iron and the cathode carbon. A very rapid evolution of gas was observed at the cathode, the level in this compartment again falling, a drop of 1.8 cm. taking place during the run. The values of pH were:-

	Anode.	Centre.	Cathode.
Before	5.0	2.5	5.0
After	4.0	6.0	10.0

The final temperature of the centre section was 46°C. A white, flocculent precipitate was seen to have formed in the cathode section, mainly on the diaphragm and electrode surfaces.

Test 4.

10 ml. of 0.5N. sulphuric acid were added to the centre compartment, the charge being 5.00 g. of dolomite. The liquid movement was again from cathode to centre, a drop of 2.1 cm. being recorded in 25 minutes. The final values of pH were:-

<u>Anode</u>: 5.0 <u>Centre</u>: 6.8 <u>Cathode</u>: 10.0

The final temperature of the centre section was 44°C. A precipitate, similar to that obtained in the previous test, formed in the cathode compartment. Contamination caused by iron from the anode was again noted.

Test 5.

A charge of 5.00 g. of half-calcined dolomite was used/

used, suspended in distilled water. Flow was from anode to centre. After 30 minutes the pH values were:-

Anode: 5.0 **Centre**: 10.0 **Cathode**: 8.0

Test 6.

10 ml. of 0.5N. hydrochloric acid were added to the centre section before addition of the charge of 5.00 g. of half-calcined dolomite. The iron electrode was replaced by one of carbon. An immediate evolution of gas was noted in both outer compartments on closing the circuit. Final pH values were:-

Anode: 3.0 **Centre**: 10.0 **Cathode**: 10.0

A solid settled out in the cathode section of a more granular character than those precipitates previously obtained.

The results of analysis of cathode liquids are given in Table III.

TABLE III.

Preliminary Tests 1 - 6

Test No.	App.Pot. (Volts)	Initial current (amps)	Final Current (amps)	Analysis of Cathode Liquid		
				Ca(mg)	Mg(mg)	Ratio Ca/Mg
1	225	0.05	0.08	-	-	-
2	190	0.35	0.10	-	-	-
3	100	0.95	0.18	12	1	12.0
4	195	0.30	0.33	9	2	4.5
5	230	0.12	0.03	3	2	1.5
6	240	0.10	0.20	29	2	14.5

The preliminary tests were completed by carrying out a series of runs in an attempt to achieve reproducible results. In each test, 5.0 gm. of half-calcined Duror dolomite were suspended in distilled water in the centre compartment, the outer compartments also being filled with distilled water. 10 ml. of 0.5N. Sulphuric acid were added to the centre compartment.

Four such tests were made. It was observed that electro-osmotic flow varied in direction from one test to another and that values of resistance were not in good agreement. Since all other factors were the same, it was decided that the differences must be derived from the diaphragms. Resistance could be altered depending upon whether or not the diaphragm was partially clogged with precipitated solid, while the direction of the electro-osmotic flow could be altered by the charge on the diaphragm.

Two further runs were made in which the diaphragms were soaked in 5N. sulphuric acid and rinsed with distilled water before commencement. Very heavy currents at the beginning of the tests, however, showed that residual acid was present in the diaphragms. Additionally, a rather larger amount of alumina was found in the cathode section than normally. Conditions of flow and resistance were much closer.

Two final tests were made in which the diaphragms after soaking in acid were then placed in position and distilled water/

water allowed to seep through. This was repeated with a second lot of distilled water. The tests made using these diaphragms gave good agreement.

Discussion of Results of Preliminary Tests.

The first test showed that, when no chemical reagent was present to assist the dissolution of the mineral, there was very little action. Contamination of the material with iron from the electrodes was observed, an interesting point being that iron produced outside the cathode section did not pass through the cathode diaphragm, apparently being precipitated entirely at the diaphragm because of the alkalinity in this region.

Electro-osmotic flow was reduced or completely inhibited when acid was added to the suspension. It was also reduced by the formation of a hydrostatic head, acting against it, in the compartment to which the water flowed.

The addition of acid, hydrochloric or sulphuric, assisted the migration of calcium and magnesium to the cathode section.

In analysing the contents of the cathode chamber, it was found that aluminium was present, especially when acid had been used. This was presumably derived from alumina in the diaphragm and in every analysis a preliminary precipitation of aluminium, using ammonium hydroxide, was made.

Reproducibility of tests was not good, a major point of/

of difference being the direction of liquid flow. It is thought that this must have been due to the diaphragm being in various states of charge at the commencement of tests, depending on whether or not acid had been used previously. An attempt to rectify this by soaking the diaphragms in acid prior to the start of a test was unsuccessful because of the very high currents which were produced and also because of the rather large amount of alumina dissolved from the diaphragms. Soaking in acid followed by soaking in distilled water remedied this difficulty.

Difficulties in experimental procedure were found to exist. Stirring was inefficient in the centre section because of its rectangular shape. Insertion and removal of diaphragms was a major operation and the avoidance of leaks at the edges of the diaphragms was not at all easy. The electrical circuit was not at all satisfactory from the point of view of control and measurement.

These considerations led to the design and construction of Electrodialytic Cell II (Figures 2 and 3) and Electrical Circuit II (Figure 10).

Tests on Modified Cell.

The cell was filled to the overflow level with water and/

and a potential applied.

In practice, the only difficulty encountered was leakage at diaphragms. Liquid was found to be seeping from the edges and this was prevented by painting these edges with a waterproof porcelain paint, "Porcenam."

It was observed that the electro-osmotic flow decreased through time and, on examination of the cathode diaphragm, a stain of ferric hydroxide was found.

The addition of acid was again seen to inhibit the electro-osmotic flow.

INVESTIGATION OF THE POSSIBILITY OF SEPARATING CALCIUM AND MAGNESIUM BY ELECTRODIALYSIS OF MIXTURES OF THEIR CARBONATES.

1. Without Addition of Acid.

Tests were made (W1-W6) in which a suspension of calcium carbonate and heavy magnesium carbonate in distilled water was electrodialysed for 60 minutes at increasing voltages. The suspension, which consisted of 0.500 g. of each carbonate in 200 ml. of water, was contained in the centre section of the cell, each outer section holding 140 ml. of distilled water.

The results are shown in Table IV.

TABLE IV.

Data From Tests W1 - W6.

Test No.	Applied Potential (Volts)	Initial Current (amps)	Final Current (amps)	Volume of Liquid transferred by Electro-osmosis (ml)
W1	40	0.005	0.015	30
W2	80	0.005	0.020	65
W3	120	0.010	0.025	105
W4	160	0.010	0.035	110
W5	200	0.015	0.035	60
W6	225	0.015	0.080	175

Flow was to the cathode in all cases. The cathode diaphragm appeared to be becoming clogged as the runs proceeded, causing an uneven flow of liquid, leading to a rise in the level of liquid in the centre compartment, which apparently was receiving liquid more rapidly from the anode chamber than it was losing it to the cathode space. In Test 5 this effect was so marked that the test had to be discontinued after 30 minutes to prevent the liquid in the centre section from overflowing.

Before starting Test 6, the cathode diaphragm was soaked in dilute acid and then in distilled water. It will be seen that this treatment improved the porosity of the diaphragm considerably, there being only a slight increase in level in the centre compartment during Test 6.

Analysis of the cathode liquids from these tests showed the presence of only traces of calcium and magnesium.

In all tests the pH of the anode section became acid and that of the cathode alkaline, the effect being greater at higher voltages.

2. Effect of addition of sulphuric acid.

Tests were made (A1-A9) using sulphuric acid to promote attack, this particular acid being chosen on consideration of the relative solubilities of calcium sulphate (sparingly soluble) and magnesium sulphate (readily soluble) in water. The results of the tests are given in Table V.

The/

TABLE V.

Tests A1 - A9.

Test No.	Acid Added		Applied Potential (volts)	Current (amps)		Analysis of Cathode Liquid			
	Amounts (ml)	Strength		Initial	Final	Ca(mg)	Mg(mg)	Total (mg)	Ratio Ca/Mg
A1	10	N	40	0.10	0.18	28	7	35	4.0
A2	10	5N	40	0.26	0.45	43	24	67	1.8
A3	50	5N	40	0.34	0.44	55	42	97	1.3
A4	10	5N	40	0.50	0.20	74	36	110	2.1
A5	10	5N	40	0.42	0.80	38	22	60	1.7
A6	10	5N	40	0.70	0.80	16	-	16	-
A7	50	5N	20	1.50	2.10	43	17	60	2.5
A8	50	5N	15	3.20	2.50	41	15	56	2.7
A9/1	50	5N	15	2.20	2.15	7	-	7	-
A9/2	50	5N	15	1.90	2.25	22	11	33	2.0

The duration of all the tests was 1 hour except where otherwise stated. The solid was placed in the centre section in all cases excepting those runs in which a two-compartment cell was used, when the solid was placed in the anode chamber. The amounts used were 0.5 gm. of each carbonate unless otherwise stated. The suspending medium was distilled water, volumes used being:-

Anode section: 140 ml. Centre section: 200 ml.
Cathode section: 140 ml.

When only two compartments were used, the volumes were:-

Anode section: 400 ml. Cathode section: 140 ml.

The electrodes were of carbon and were placed 3.75" apart in each test.

Details of individual runs.

A1. Reversal of flow, which had been towards the cathode, took place towards the end of the test. It was noted that the resistance of the cell passed through a minimum while flow occurred to the cathode, beginning to rise again while flow was indeterminate and dropping again when reversal of flow occurred.

A2. Stronger acid was used in this test. No reversal of flow was observed but it was noted that, while the resistance passed through a minimum, it did not reach a maximum before the end of the test.

A3. An increased amount (5.0 gm.) of each carbonate was used in this test, and additions of acid were made to the centre/

centre compartment at intervals. Reversal of flow occurred and similar fluctuations of resistance to those in A1. were observed.

<u>A4</u>. This test was of 3 hours' duration. No reversal of flow was seen. The behaviour of the resistance was similar to A2.

<u>A5</u>. For this test the cell was converted to one of two compartments by removing the anode diaphragm. In this way it was hoped to conserve the effect of the acid on the suspension. No reversal occurred; the resistance falling to a minimum value and remaining steady at this value until the end of the test.

<u>A6</u>. The duration of this test was 15 minutes, conditions otherwise being as in A5. Flow and resistance were found to be as in A5.

<u>A7</u>. This test was made as for A5., but using a much larger amount of acid. A low value of resistance was obtained and, to reduce the heavy current, an applied potential of 20 volts was used. No reversal of flow took place, the resistance again dropping to a minimum value and remaining steady at that value until the end of the test.

<u>A8</u>. Similar conditions to those of A7 were employed except that the acid was left in contact with the solid for 15 minutes before the electrodialysis was commenced. The resistance was very low and the applied potential was reduced to 15 v. Once again flow was towards the cathode throughout the test.

A9. As in A8., except that after 15 minutes the cathode liquid was replaced with distilled water and the test continued for a further 45 minutes. Again the potential applied was 15V, resistance being as in A8. The cathode sample after 15 minutes is referred to as A9/1 and that after the second period of 45 minutes as A9/2. Electro-osmotic flow was again towards the cathode.

Observations on Tests A1 - A9.

1. Ca/Mg ratio appears to be lower when a greater amount of solid is transferred to the cathode compartment. This would seem to indicate that the calcium ions are the first to migrate and that they migrate faster, or that they are less strongly adsorbed than the magnesium ions.

2. No important differences were found in the results obtained using a two-compartment and a three-compartment cell. It should be noted, however, that there was an excess of acid present originally.

3. There appears to be no tendency for a change in the rate of transference of ions between the beginning of a test and the end, except that the rate may be reduced latterly due to the diaphragm becoming clogged with precipitated solid.

4. The use of a delay period before commencing the test had no apparent effect on the amount of material transferred but had the effect of making the cathode section acid, due presumably to the presence of free acid in that compartment at the start of the test.

5. Reversal of electro-osmotic flow was noticed in some tests in which a three-compartment cell was used. It is thought that this must be due to a difference in the charge of the diaphragms caused either by the change in conditions of pH in their vicinity or by the adsorption of anions and cations as they migrate. The behaviour of the resistance during such a change is shown in Figure 12 (A), in which resistance/time curves are also given demonstrating steady unidirectional flow (B) and flow tending towards a point of reversal (C).

Reversal of flow was accompanied by a fall in resistance, this having increased during a period of indeterminate flow.

Steady flow was typified by a steady, minimum value resistance.

Building up of the resistance indicated a tendency towards a point of reversal.

Since the porous earthenware diaphragms became clogged with precipitated solid and since the use of acid caused contamination of the cathode liquid, presumably with aluminium dissolved from the diaphragm, it was decided to test a number of cellulosic diaphragms for suitability in the electrodialytic tests.

Use/

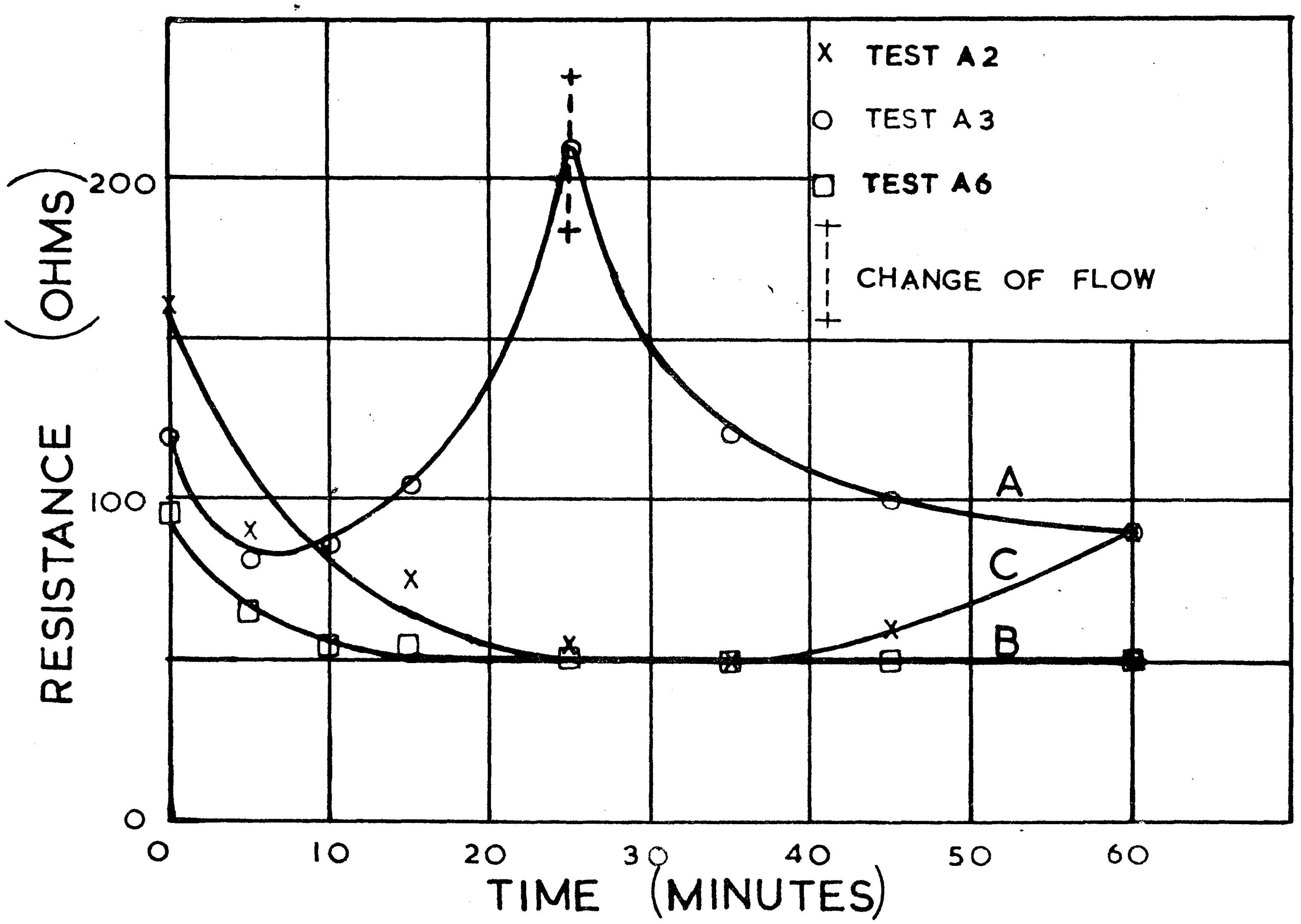

X TEST A2
O TEST A3
□ TEST A6
+--+ CHANGE OF FLOW
A
B
C
RESISTANCE (OHMS)
0
100
200
0
10
20
30
40
50
60
TIME (MINUTES)

FIGURE 12.

Use of Cellulosic Diaphragms.

Electrodialytic tests were made using diaphragms of cellulose acetate, cellophane, and parchment paper, to determine whether or not any of these materials were suitable for application to the present investigation.

The diaphragms were first tested for resistance to water and to sulphuric acid. It was found that all three were unaffected by immersion in water and in 5N. sulphuric acid for periods up to 6 hours at least. The diaphragms were then used in electrodialysis of a suspension of the mixed carbonates in acidified distilled water.

Cellulose Acetate. No electro-osmotic flow was observed, the resistance of the cell remaining at a high value throughout the 30 minutes' test. No solid was found in the cathode section.

Cellophane. The resistance of the cell was seen to decrease during a preliminary test and a further test was made in which 0.5 gm. each of calcium and heavy magnesium carbonate were suspended in 400 ml. of distilled water in the anode section of a two-compartment cell, the cathode section containing 140 ml. of distilled water. 50 ml. 5N. sulphuric acid were added to the anode compartment and a potential of 20V. applied. The resistance of the cell dropped and appeared to be steadying when the test was terminated after 1 hour. A slight electro-osmotic flow to the cathode was observed. On examination of the liquid from the cathode compartment/

compartment, it was found that the amount of solid present was negligible.

Parchment paper. Once again, a preliminary test showed that resistance gradually decreased during the run and a test exactly as for Cellophane was made. In this case no electro-osmotic flow was observed, the resistance falling slowly throughout the hour which the test lasted.

The cathode liquid again showed only a very small amount of solid residue on evaporation to dryness.

These materials, therefore, seemed unsuitable for use in the electrodialysis of suspensions of inorganic materials to which acid had been added.

It would be expected that the very much lower porosity of these diaphragms would reduce the amount of calcium and magnesium migrating to the cathode but it is thought that the probable explanation of the almost non-existent transference is that the hydrogen ions, being much smaller and moving much faster, utilise the available space of the diaphragm to the almost complete exclusion of the larger calcium and magnesium ions.

Effect of Increasing Amount of Solid in Suspension.

Three tests (C1-C3) were made under standard conditions and the amount of solid in suspension altered in each test to find the effect of increasing concentration. Equal amounts of calcium and heavy magnesium carbonates were used, suspended in/

in 400 ml. of distilled water in the anode section of a two-compartment cell, the cathode space containing 140 ml. of distilled water. 10 ml. of 5N. sulphuric acid were added to the anode section and a potential of 40V. applied for 1 hour.

The results are shown in Table VI.

The ratio Ca/Mg. here was lower when a greater amount of material had migrated, again inferring that the magnesium was more slowly electrodialysed than the calcium.

The amount of material transferred appeared to decrease when a greater concentration of solid was used.

Effect of Adding an Increased Amount of Acid.

Three tests were made (CA1 - CA3) exactly as in C1 - C3 except that 50 ml. of 5N. sulphuric acid were added in each case. The results are shown in Table VII.

It will be seen that the increased amount of acid has little effect, except for CA3 in which the amount of magnesium transferred is high compared to the amount found in C3.

Since the amounts of calcium and magnesium transferred to the cathode were so small, it was thought better to try to find the causes and, if possible, a solution, since it was fairly certain that the various factors being investigated were overshadowed by others which prevented the variations from showing.

Consideration of Possible Causes of Interference with Electrodialysis.

A number of reasons suggest themselves as possible sources of hindrance to electrodialysis.

(a)Polarisation.

Polarisation of the cathode by the hydrogen evolved there would cause an increased resistance in the cell. Observation showed that a "barrier" of large gas bubbles formed in the space between the cathode diaphragm and the cathode, leading to increased resistance.

(b)Ionic pressure.

The effect of the ions already present in the cathode liquid would be to hinder further transference from the anode section. This factor was not thought likely to be of importance in the present problem, since the amounts of ions in the cathode liquid are so small.

(c)Precipitation of solid in the cathode diaphragm.

It had been observed from the initial tests onwards that the cathode diaphragm became less porous as the test proceeded. This is undoubtedly due to precipitation of solids on the surface and in the pores of the diaphragm. Ferric hydroxide has been seen to be precipitated on the surface of the diaphragm away from the cathode and it has been found necessary to soak the diaphragms in acid after each test to clear them of such material. The alkalinity of the liquid in/

in the region of the cathode diaphragm is the cause of the precipitation and prevention could only be effected by avoiding this high value of pH, i.e., by keeping the cathode liquid neutral or even acid during a test.

Tests were made to examine each of these points, the results of which are given in Table VIII.

(a) Polarisation.

The object was to disperse the hydrogen evolved at the cathode and so prevent it forming a barrier to the passage of ions. It had been shown during a previous test that if the layer of large gas bubbles between the cathode diaphragm and the cathode was swept away by a jet of water, the resistance fell rapidly, only to rise again when the gas layer reformed.

It was thought that a surface-active agent such as ethyl alcohol would reduce the interfacial tension and prevent the formation of large bubbles.

A test (P1) similar to C1 was made in which ethyl alcohol was allowed to drip continuously into the space between the cathode diaphragm and the cathode. Only small bubbles of hydrogen formed and the resistance of the cell was somewhat lowered. Analysis of the cathode liquid showed that there was an increase in the amount of both calcium and magnesium transferred compared to C1.

(b)/

TABLE VIII.

Attempts to increase Electrodialysis.

Test No.	Current(amps).		Analysis of Cathode Liquid			
	Initial	Final	Ca(mg)	Mg(mg)	Total (mg)	Ratio Ca/Mg
P1	0.30	0.26	50	29	79	1.7
D1	0.40	0.26	24	2	26	12.0
R1	0.18	0.06	2	6	8	0.3
F1	1.00	0.30	11	6	17	1.8
B1	0.27	0.55	48	22	70	2.2
B2	0.50	0.60	25	9	34	2.8
B3	0.45	0.40	25	13	38	1.9
B4	0.34	0.32	68	6	74	11.3
E1	0.40	0.60	29	13	42	2.2
E2	0.10	0.60	32	32	64	1.0

(b) Ionic Pressure.

In this case a test (D1) similar to C1 was made, draining the cathode section every 10 minutes and re-filling it with distilled water, the duration of the test being 40 minutes.

Two further tests were made involving the replacement of the cathode liquid. In the first (R1), a constant overflow was produced by allowing distilled water to run continuously into the compartment at a rate of about 10 ml./minute. The test was otherwise the same as C1. The resistance increased gradually during the test and was never as low as in C1.

In the second test (F1), which was otherwise the same as the first, 50 ml. of distilled water were added to the cathode chamber every 10 minutes to cause a partial flushing of the section. The resistance was considerably lower than in the previous test but again tended to increase.

Changing of the liquid in the cathode section either by complete renewal, constant overflow, or periodic flushing has thus been unsuccessful, the increased resistance of the fresh distilled water more than nullifying the effect of removing the ions present in the cathode space.

(c) Clogging of Cathode Diaphragm - Use of buffer solutions.

(i) A test (B1) similar to C1 was made in which the cathode section was filled with a buffer solution of pH 6.5 instead of distilled water. The resistance of the cell was lower than before/

before, tending to reach a steady value. As the test proceeded, the pH of the cathode section gradually became higher and after 30 minutes was distinctly alkaline, presumably due to electrolytic dispersion of the buffer solution.

(ii) Since the use of a buffer solution had had the desired effect of permitting the transference of a reasonable amount of ions to the cathode while draining the cathode had caused further hindrance, a test was made in which the cathode section was filled with buffer solution and the buffer solution replaced at regular intervals.

The test (B2) was again similar to C1, buffer solution of pH 6.5 being used in the cathode, which was drained and re-filled every 10 minutes. The resistance was again low and tended to reach a steady value.

(iii) A test (B3) was made as in (i) except that both the anode and cathode sections were filled with buffer solution of pH 6.5. The resistance dropped gradually over a period of 25 minutes at which point the buffering action had virtually ceased, the resistance rising again until the end of the test. It was noted that during the greater part of the run there was no formation of a layer of large gas bubbles between the cathode diaphragm and the cathode.

(iv) A final test (B4) was made using 5.0 gm. of each carbonate suspended in distilled water in the anode section, 10 ml. of 5N. sulphuric acid being added. The cathode section was filled with buffer solution of pH 6.5 and 50 ml. added every 10 minutes to cause a partial flushing of the compartment, the duration of the test being 40 minutes. The resistance maintained a steady value throughout the run, being a little higher than in (iii).

Observations on tests using buffer solutions.

The use of a buffer solution of pH 6.5 in the cathode compartment allowed the migration of amounts of calcium and magnesium which, although still not very large, are considerably more than those of other tests.

Draining and re-filling the cathode section at intervals hindered the migration of cations.

Filling both the anode and cathode compartments with buffer solution gave smaller amounts of calcium and magnesium transferred to the cathode section.

Using a larger amount of solid in suspension and adding buffer solution in 50 ml. portions at regular intervals to the cathode section gave a good result, much more calcium than magnesium being transferred to the cathode chamber.

During tests the buffering action was dissipated presumably because of electrolysis of the buffer solution.

Use of acid.

(i) A test (E1) similar to C1 was made in which dilute sulphuric/

sulphuric acid was allowed to drip on to the top surface of the cathode diaphragm throughout. The resistance of the cell decreased during the run, there being no gas layer in the cathode section.

(ii) In a further test (E2) 5.0 gm. of each carbonate were suspended in the anode section, all other conditions being as previously. In this case, the resistance did not decrease as rapidly as in the first test.

Use of Ammonium Chloride Solution as Suspending Medium.

It was hoped that the ammonium chloride would take up the calcium by complex formation, when it would be possible that the overall charge on the complex ion would be negative, thus preventing migration of the calcium to the cathode.

(i) AC-1. 5.0 gm. of each carbonate were suspended in a 2% solution of ammonium chloride in the anode section, the cathode chamber being filled with buffer solution of pH 6.5 and 50 ml. of buffer solution added every 20 minutes, the applied potential being 40 V. After 30 minutes the buffer ceased to be effective and the resistance immediately began to rise, the test being terminated after 40 minutes.

(ii) AC-2. This test was the same as (i) except that the suspension was stirred for 15 minutes before commencing electrodialysis in order to let the reaction take place between the calcium and the ammonium chloride. The resistance was again very/

very low, but when the buffer ceased to be effective after 20 minutes, it again increased.

(iii) AC-3. In this case the suspension was stirred for 30 minutes before commencing electrodialysis. The behaviour of the buffer solution and of the resistance was observed to be very similar to the previous test.

(iv) AC-4. A test was made under the same conditions as in (ii), i.e., allowing 15 minutes before commencing electrodialysis, but using 4% ammonium chloride solution. The resistance was even lower in this instance, rising in value when the buffer solution ceased to be effective after about 15 minutes.

(v) AC-5. For this test a suspension of 5.0 gm. each of calcium carbonate and magnesium oxide in 2% ammonium chloride was used, 30 minutes being allowed to elapse before electrodialysis was commenced. Other experimental conditions were as before. The resistance was a little higher on this occasion. The results of these tests are given in Table IX.

Observations on tests using ammonium chloride solutions.

The amount of material transferred was again low, but the effect of causing more magnesium than calcium to migrate was achieved. It was found necessary to allow a period of time to elapse before commencing electrodialysis, indicating that some complex formation was taking place. Use of a stronger solution of/

TABLE IX.

Tests AC1 - AC5.

Test	Current(amps).		Analysis of Cathode Liquid.			
No.	Initial	Final	Ca(mg).	Mg(mg).	Total(mg).	Ratio Ca/Mg.
AC 1	1.2	0.24	6	2	8	3.0
AC 2	1.3	0.32	5	7	12	0.7
AC 3	0.9	0.33	4	8	12	0.5
AC 4	1.6	0.65	10	6	16	1.7
AC 5	1.9	0.43	4	9	13	0.4

of ammonium chloride reversed the effect, more calcium than magnesium migrating to the cathode. A very slightly improved separation was obtained using a mixture of calcium carbonate and magnesium oxide.

Addition of Carbon Dioxide.

If a stream of carbon dioxide gas is bubbled into a suspension of the mixed carbonates, magnesium should be rendered soluble as the bicarbonate.

(i) G1. 5.0 gm. of each carbonate were suspended in distilled water in the anode section of the cell, the cathode chamber being filled with buffer solution of pH 6.5, 50 ml. of buffer solution being added every 10 minutes. Carbon dioxide gas was bubbled into the anode compartment during the test. The resistance dropped steadily as the run proceeded and a slight flow to the cathode was observed.

The amount of material which had migrated was small but the desired effect had been produced, i.e., more magnesium than calcium had migrated to the cathode chamber.

The formation of the soluble bicarbonate of magnesium is achieved more readily from dolomite which has been half-calcined to give a mixture of calcium carbonate and magnesium oxide and a test similar to the previous one was made, using a mixture of Analar calcium carbonate and Analar magnesium oxide to simulate this.

A/

A modified apparatus (Figure 4), circular in form, was used for this test, as a preliminary to the eventual use of an apparatus in which the anode and cathode liquids would be constantly circulated.

(ii) G2. 1.5 gm. each of magnesium oxide and calcium carbonate were suspended in 150 ml. of distilled water in the anode (inner) section, the cathode (outer) section containing buffer solution; carbon dioxide gas being passed into the suspension and 50 ml. of buffer added to the cathode chamber every 10 minutes, immediately after 50 ml. of the cathode liquid had been siphoned off. The resistance rose throughout the run.

The result was an improvement on that obtained in the rectangular cell and was the best separation obtained so far. It was decided to investigate this further and tests were made using a new electrodialytic cell.

It had already been shown that cellulosic diaphragms were useless when acid was used to attack the mineral suspension but it was thought that such membranes should be quite efficient when carbon dioxide was the chemical reagent since there would be no large concentration of interfering ions present.

A small glass cell (Figure 5) was designed and built, suitable for use with cellulosic diaphragms. Two tests were made to find the relative effects of carbon dioxide on the electrodialysis of dolomite and of half-calcined dolomite and a/

a third to determine whether or not successive treatments would yield further separation.

G3. 5.0 gm. of Duror dolomite (ex 300 mesh B.S.S.) were suspended in 100 ml. of distilled water and CO_2 bubbled through for 2 hours. The suspension was then transferred to the centre section of the electrodialytic cell, the outer compartments being filled with distilled water. The diaphragms used were of regenerated cellulose. The current rose from an initial value of 0.015 amps. to 0.028 amps. The centre section became slightly acid as the test proceeded while the anode and cathode compartments rapidly became very acid and very alkaline respectively. There was a slight electro-osmotic flow to the cathode chamber.

G4. A second test was made exactly as above except that 5.0 gm. of half-calcined Duror dolomite were used, the same pre-treatment being given. During electrodialysis the current rose from an initial value of 0.03 amp. to a final value of 0.05 amp. Electro-osmotic flow to the cathode was observed and the liquid in the cathode chamber became decidedly cloudy with finely precipitated solid. The centre section gradually became slightly alkaline while the anode and cathode compartments rapidly became very acid and very alkaline respectively.

G5. The suspension from the centre compartment of the cell used in the previous test was again treated with carbon dioxide/

a third to determine whether or not successive treatments would yield further separation.

G3. 5.0 gm. of Duror dolomite (ex 300 mesh B.S.S.) were suspended in 100 ml. of distilled water and CO_2 bubbled through for 2 hours. The suspension was then transferred to the centre section of the electrodialytic cell, the outer compartments being filled with distilled water. The diaphragms used were of regenerated cellulose. The current rose from an initial value of 0.015 amps. to 0.028 amps. The centre section became slightly acid as the test proceeded while the anode and cathode compartments rapidly became very acid and very alkaline respectively. There was a slight electro-osmotic flow to the cathode chamber.

G4. A second test was made exactly as above except that 5.0 gm. of half-calcined Duror dolomite were used, the same pre-treatment being given. During electrodialysis the current rose from an initial value of 0.03 amp. to a final value of 0.05 amp. Electro-osmotic flow to the cathode was observed and the liquid in the cathode chamber became decidedly cloudy with finely precipitated solid. The centre section gradually became slightly alkaline while the anode and cathode compartments rapidly became very acid and very alkaline respectively.

G5. The suspension from the centre compartment of the cell used in the previous test was again treated with carbon dioxide/

dioxide, the gas being bubbled through for a further two hours. The suspension was replaced in the centre compartment and electrodialysis carried out as before except that non-waterproof Cellophane diaphragms were used and the test terminated after 60 minutes. The centre section remained slightly alkaline throughout while the anode and cathode sections became very acid and very alkaline respectively. The current rose from an initial value of 0.025 amp. to a final value of 0.075 amp. Again, electro-osmotic flow to the cathode was observed while the cathode liquid became cloudy with precipitated solid.

Results of these tests are given in Table X.

<u>Observations on tests using carbon dioxide</u>.

The initial test showed that, while the amounts of calcium and magnesium migrating were small, the desired effect of causing more magnesium than calcium to migrate to the cathode chamber had been achieved. The test made in the circular cell gave an even better separation although the amounts involved were again very small. The tests made using cellulosic diaphragms showed that the half-calcined dolomite gave a much greater transference of magnesium relative to calcium while on further treatment an even better separation was achieved.

TABLE X.

Tests G1 - G5.

Test No.	Applied Potential (Volts)	Current (amp)		Duration of test (mins)	Analysis of Cathode Liquid.			
		Initial	Final		Ca (mg)	Mg (mg)	Total (mg)	Ratio Ca/Mg
G1	40	0.1	0.37	40	8	12	20	0.7
G2	40	0.9	0.30	40	2	25	27	0.08
G3	230	0.02	0.03	90	10	-	10	-
G4	230	0.03	0.05	90	2	15	17	0.13
G5	230	0.05	0.08	60	-	29	29	-

Circulating Electrodialytic Cell.

The cell which is shown in Figure 6 was designed after consideration of the results of all the previous tests. It was hoped that the constant circulation of both anode and cathode liquids would help to prevent clogging of the diaphragm.

Although it was known that the test most likely to give the best separation of magnesium from calcium would be the electrodialysis of half-calcined dolomite which had been treated with carbon dioxide gas, it was decided for the sake of completeness to do also a test using sulphuric acid and one using ammonium chloride.

Use of Sulphuric acid.

H1. 15 gm. of half-calcined Duror dolomite were suspended in 1400 ml. of distilled water in the anode chamber of the circulating electrodialytic cell, 1400 ml. of a buffer solution of pH 6.5 filling the cathode chamber. 10 ml. of 5N. sulphuric acid were added to the suspension in the anode section, both anode and cathode contents being circulated continuously.

The resistance of the unit was very low and decreased slightly over the first 15 minutes of the test. From this time the buffering action began to fail, the pH of the cathode section gradually rising while the resistance also began to increase slightly. A definite cloudiness developed in the cathode/

cathode liquid due to precipitated solid.

Use of Ammonium chloride solution.

H2. 15 gm. of half-calcined Duror dolomite were stirred in 150 ml. of 4% ammonium chloride solution for 2 hours prior to the test. The suspension was then transferred to the anode section and distilled water added to make a total volume of 1400 ml. The cathode chamber contained 1400 ml. of a buffer solution of pH 6.5. The resistance of the unit was very low but increased slightly as the buffer began to fail in the later stages of the run.

Use of Carbon Dioxide.

H3. 15 gm. of half-calcined Duror dolomite were suspended in 150 ml. of distilled water and carbon dioxide gas bubbled through for 2 hours. The suspension was then transferred to the anode section of the cell and the total volume made up to 1400 ml. with distilled water, the cathode space containing 1400 ml. of a buffer solution of pH 6.5. The resistance of the cell was very low but increased slightly as the effect of the buffer began to cease.

Results of these tests are given in Table XI.

Observations on tests made using the circulating electrodialytic apparatus.

In all three tests the amount of magnesium transferred was greater than the amount of calcium, even with sulphuric acid as the chemical reagent.

As was hoped, the last test using a suspension of half-calcined dolomite, pre-treated with carbon dioxide, gave the best separation and greatest amount of magnesium yet made to migrate.

TABLE XI.

Tests H1 - H3.

Test No.	Applied Potential (Volts)	Current(amps)		Duration of test (mins)	Chemical reagent used	Analysis of Cathode Liquid.			
		Initial	Final			Ca (mg)	Mg (mg)	Total (mg)	Ratio Ca/Mg.
H1	12	1.40	1.15	45	H_2SO_4	44	152	196	0.29
H2	4	0.70	0.65	45	NH_4Cl	52	56	108	0.93
H3	6	1.00	0.85	60	CO_2	12	344	356	0.04

Electrodialysis of Adsorbed Calcium and Magnesium.

Previous tests had shown that calcium appeared to be adsorbed less strongly than magnesium and an investigation was made of the possibility of using this as a means of separation.

A material was required which, ideally, would adsorb both calcium and magnesium ions strongly in order that a simple washing with water would not remove the adsorbed ions. If such a material could be found, it might be possible to electrodialyse a suspension of it after adsorption of the ions so that calcium would be stripped off preferentially, leaving the magnesium to be recovered at a later stage, by an acidwash for example.

A firm dealing with such materials was approached but was unable to suggest any type of material which would be suitable.

It was decided, therefore, to experiment with kieselguhr, although it was not thought very practicable since this material was unlikely to have the desired properties.

(i) Adsorption.

A charge of kieselguhr, supported on a circle of wire gauze, was formed in an adsorption column and solutions of calcium and magnesium salts were allowed to percolate. The/

The kieselguhr was then packed into a glass tube fitted with a stainless steel gauze electrode at either end and a potential applied.

It was hoped that an electro-osmotic flow would be set up towards the cathode which would enhance the removal of adsorbed ions. Severe electrolytic disturbances, however, rendered the experiment impracticable. This was attributed to the presence of acid remaining in the kieselguhr after adsorption. Since it was not possible to wash out the acid without removing the metal cations, this system was abandoned.

A further test was made in which the treated kieselguhr was electrodialysed in the centre compartment of the cell shown in Figure 5, using non-waterproof Cellophane diaphragms.

50 ml. of a solution of calcium chloride, containing 0.22 g. of calcium/100 ml., and 50 ml. of a solution of magnesium oxide, containing 0.32 g. magnesium/100 ml. were allowed to percolate through a column of 15 g. of kieselguhr. After the adsorption process, the kieselguhr was suspended in 100 ml. of distilled water and electrodialysed for 1 hour at a potential of 230 V. The current rose steadily throughout, the anode and cathode sections becoming distinctly acid and alkaline while the centre compartment retained its original/

original acidity. Analysis of the cathode liquid showed the presence of 0.011 g. of calcium and a negligible amount of magnesium.

This result was in accordance with expectations but, once again, the amounts involved were very small and, as was suspected, kieselguhr is not a particularly suitable medium.

DISCUSSION OF RESULTS AND CONCLUSIONS.

Practical Details.

(a) Electrodialytic Cells.

(i) Materials of construction.

The materials which have been used in the construction of the electrodialytic cells employed are Perspex and glass, except in the circulating cell (Figure 6) in which the carbon cathode forms the cell wall.

Perspex, while capable of wide application, has the disadvantages of being very readily affected by heat or even by excessive strain, causing leakage. This was specially noticeable in Cell II (Figures 2 and 3), the flanges gradually becoming distorted and leaks developing here and at other points where sections had sprung to some extent.

Glass, while it does not suffer from this fault, gives difficulty in the making of a watertight seal. If a flange is desired, it becomes necessary to grind the glass faces to

a/

a perfectly flat surface.

Since the cell is normally sectional the methods of securing the various sections must be compared.

Perspex can be flanged, the flanges tapped and the sections held by screwing them together. Glass, on the other hand, can not be treated in this way and some system of tension must be incorporated, such as a series of springs so placed that they force the sections together.

In designing Cell IV (Figure 5), however, these disadvantages were overcome fairly simply by using rubber bungs as shown. A watertight joint was obtained and the cell could be easily dismantled.

(ii) <u>Shape of the cell</u>.

The rectangular shape of Cells I and II was found to be not altogether suitable. The centre section had to be square in form if efficient agitation was desired. These cells had the advantage that the separation of the electrodes could be altered at will while in Cell IV a series of centre sections of varying length would have to be employed. The circular cell, however, was better from the point of view that the diaphragm area, being smaller than that of the outer section, could be covered completely by an electrode and yet leave enough space for circulation of liquid in these sections. In the rectangular cells, the electrodes tended to block the free movement of material in the outer sections.

Cell/

Cell III(Figure 4) with electrodes and diaphragm circular anc concentric showed the way to the construction of Cell V (Figure 6), in which the need for an outer cell wall was obviated, the carbon cathode being used.

A final point in favour of the round cell is the fact that its closed nature and shape make circulation easier.

(iii)Special features.

Cell I, the prototype, was used to discover the points which would have to be considered in designing further cells.

The main factors which emerged were:

1. The centre section must be square to allow efficient agitation.
2. Overflow outlets were required in each compartment to prevent the building up of a hydrostatic head.
3. The cell had to be sectional and easy to assemble and dismantle.

All of these points were incorporated in Cell II.

Cell IV had the advantage of being constructed in glass rather than in Perspex, the rubber rungs serving the double purpose of securing the diaphragms and providing a watertight join between sections.

Cell IIIwas used as a forerunner of Cell V and as such/

such was not by any means perfect in itself. Once again the question of joining compartments was encountered and was here solved by using a pot as the diaphragm, the anode space being inside it and the cathode space outside.

Cell V was the final design, built to fulfil the requirements indicated by previous experiments. Its outstanding differences were:

1. The use of the cathode tube as the outer wall.
2. Circulation of both the anode and cathode liquids throughout tests.

In this apparatus, watertight joins were achieved by holding the concentric electrodes and diaphragm tightly between end-plates by means of tie-rods, the various parts fitting into rubber-gasketed recesses.

(b) Electrodes.

Iron electrodes, as used in Cell I, were found to be unsuitable because of contamination of the cell contents caused by electrolytic attack on the iron.

Carbon was a much better material but was attacked when used as anode by nascent oxygen which caused a gradual wearing away.

Platinum electrodes (Cell IV) were excellent in all respects but nickel was also subject to electrolytic attack.

(c) Diaphragms.

(i) Porous earthenware.

Such diaphragms were used in all of the electrodialytic cells except Cell IV, for which they were not suitable. Disadvantages were contamination of the cathode liquid with alumina derived from them and a tendency to become clogged.

(ii) Cellophane.

The electrodialysis of suspensions in which an acid was present proved impossible with Cellophane diaphragms, since their porosity was apparently so low that the hydrogen ions only, being smaller and faster, monopolised the diaphragm and little or no other material could migrate.

With suspensions in which the available ions were only those which it was desired to cause to migrate, Cellophane was found to be a highly suitable material, since there was no contamination derived from it and also since the diaphragms need only be used once and discarded. Resistance to acid, alkali and water immersion was good, the only disadvantage being again a tendency to become clogged.

(iii) Cellulose acetate.

This material was found to be unsuitable for use with acid, acting similarly to Cellophane while it had the further/

further fault of cracking when attempts were made to use it in Cell IV.

(iv) Parchment paper.

Behaviour exactly similar to cellulose acetate was found.

(v) Regenerated cellulose.

This was found to be very similar to Cellophane in its behaviour.

(d) Clogging of Diaphragms.

From the very first tests made it was apparent that clogging of the cathode diaphragm was going to cause trouble.

The first example of this was observed when a stain of ferric hydroxide formed on the diaphragm in the preliminary tests. Since iron electrodes were in use, it was hoped that the use of carbon would eliminate the effect.

Again, when a series of tests was made using tap water in Cell II, the rate of electro-osmotic flow to the chamber was seen to increase with applied potential until latterly when it fell away badly. A stain of ferric hydroxide was present on the diaphragm.

Using a suspension of magnesium and calcium carbonates in distilled water, clogging was again experienced but in this case there was no visible staining of the diaphragm/

diaphragm. It was observed, however, that the level of liquid in the centre compartment was rising. A test of the porosity of the cathode diaphragm after the tests showed that it had been badly impaired. It was found necessary to soak the cathode diaphragm in acid after it had been used in a test, in order to free it of precipitated solid.

Attempts were made to prevent this occurrence by the use of buffer solutions and by changing the liquid in the cathode compartment either continuously or periodically.

A slow continuous flow of water through the cathode chamber was not effective in preventing the pH in that compartment from becoming strongly alkaline, nor did draining the chamber and re-filling it with distilled water from time to time prove successful.

The addition of quantities of water at intervals to the cathode space gave an improvement which indicated that a fairly vigorous agitation might be beneficial.

The use of a buffer solution of pH 6.5 was successful in keeping the pH of the cathode section from becoming alkaline for a period, the buffering action eventually being lost due to the migration of ions away from the cathode. Further evidence supporting that already obtained regarding the use of a slow continuous flow and of periodic addition of liquid to cause a partial flushing was obtained using/

using buffer solution. Once again it was seen that the most effective method was the latter.

The application of a continual drip of acid on to the cathode diaphragm to prevent precipitation while effective to some extent, was discarded as impracticable.

Electrodialysis of Calcium-Magnesium mixtures.

(i) Without addition of chemical reagent.

There was very little transference of cations to the cathode space from a suspension of the materials in distilled water. This was to be expected since the solubility of dolomite in water is very slight and it is obviously necessary to have the constituent which it is desired to remove present in the form of ions.

Since calcium and magnesium occupy neighbouring positions in the electro-chemical series, it would not be expected that a successful separation could be effected using the very slight difference in electrical charge between the two. The decision was, therefore, taken to attempt to bring the magnesium into solution from whence it could be caused to migrate to the cathode while keeping the calcium in an insoluble form and so effect a separation.

The first point of difference in solubility noted was between calcium and magnesium sulphates, the former being only sparingly/

sparingly soluble in water while the latter is readily soluble.

(ii) Addition of sulphuric acid.

The results of tests made in which the mixture of carbonates was suspended in distilled water to which sulphuric acid had been added are shown in Table V.

Rather unexpectedly it was noted that in all cases more calcium than magnesium had been transferred. Leaving out considerations of solubility for the moment, it would thus appear that when calcium and magnesium ions are both available the calcium ions are preferentially separated. Two reasons suggest themselves in explanation.

Firstly, the calcium ions may migrate more rapidly than the magnesium ions. At first sight this seems unlikely since the latter are smaller ions, but it is known that all ions are hydrated in solution in water. Wells (211) states that all ions of positive charge are permanently hydrated in solution, the co-ordination number being 6 in the case of all ions except the largest (K^+, NH_4^+, Rb^+, Cs^+ and Tl^+) which are not hydrated, while the univalent ions are 4 co-ordinated. Thus, calcium and magnesium have the same co-ordination number but magnesium, being the smaller, will hold the hydrating ions more firmly than the calcium and will be retarded more than calcium.

Riehl and Wirths (212), in experiments involving dialysis/

dialysis through cellulosic membranes, found almost identical diffusion rate coefficients for a number of ions including calcium and magnesium. They stated that mass had no effect and that hydration tended to equalise the volumes.

The above reasoning does not, therefore, seem to be the correct explanation.

Secondly, it is possible that on reaching the cathode diaphragm, the magnesium ions are strongly adsorbed while the calcium ions, being not so strongly adsorbed, can migrate more readily into the cathode section. This theory is supported by the evidence of a number of workers, mainly derived from electrodialysis of soils etc., to remove the adsorbed cations. Mattson (123) found that the order of appearance in the cathode of cations electrodialysed from colloidal soil material was calcium, potassium and sodium, magnesium, aluminium, manganese and iron. Wilson (124), using electrodialysis in the removal of adsorbed cations from soil found that the most readily removed was potassium followed by calcium. Magnesium was removed very slowly and aluminium hardly at all. Oosugi and Aoki (125) found that when soils were electrodialysed, the order of migration to the cathode was calcium; magnesium, potassium and sodium; aluminium and iron. Puri and Hoon (127), in similar work, gave the order as sodium, potassium, calcium and magnesium

stabing/

stating that calcium was slowly removed and magnesium hardly at all, and the same authors (128) having carried out further investigation, stated that magnesium was always removed much more slowly than the other cations.

Consideration of this evidence indicates that the theory of strong adsorption of magnesium is probably the correct one and it is put forward here to explain the apparently illogical phenomenon of calcium being transferred in greater quantity and more rapidly to the cathode chamber.

(iii) Use of cellulosic diaphragms.

Because of the contamination of cathode liquids with alumina derived from the earthenware diaphragms and since these diaphragms became rather badly clogged during tests, it was decided to experiment with diaphragms of cellulosic material. It was found that Cellophane, cellulose acetate, parchment paper, and regenerated cellulose were all totally unsuitable when acid was used in the suspension. While considerable electrolysis took place, very little solid was found in the cathode section on evaporation to dryness.

The main difference between these diaphragms and those of porous earthenware is that the former are much less porous. It is thought probable, therefore, that hydrogen ions, being very small and fast relative to the calcium and magnesium ions, "crowded out" the larger ions and prevented them from migrating through the diaphragm to the cathode to a very great extent/

extent.

(iv) Use of greater concentration of solid.

Little information could be derived from tests in which greater concentrations of solid and larger amounts of acid were used. It was felt that any differences were being negatived due to the precipitation of solid in the cathode diaphragm. The amounts of calcium and magnesium migrating to the cathode were so small that it was considered better to investigate this before going further.

(v) Attempts to increase amount of migration.

The three main reasons for a low migration rate, i.e., polarisation, ionic pressure and the precipitation of material in the diaphragm have already been discussed.

The addition of ethyl alcohol to prevent the formation of a barrier of large bubbles of hydrogen between the cathode diaphragm and the cathode was successful.

Changing of the liquid in the cathode chamber by draining and re-filling with distilled water, continuous introduction of distilled water or periodic partial flushing proved unsuccessful.

Using a buffer solution of pH 6.5 as the cathode liquid was successful in that it kept the pH of that section from becoming strongly alkaline for some time. Electrolysis, however, gradually destroyed the buffering action, presumably due to migration of the ions of the buffer solution.

It/

It was observed that draining the cathode chamber and re-filling it with fresh buffer solution at intervals hindered the migration rates, as had happened with distilled water.

The use of buffer solution in both compartments also hindered the migration rates. The buffer solution is known to have only potassium and sodium as cations and it is postulated that the preferential electrodialysis of these ions, in accordance with the theories previously discussed, was the cause.

Periodic flushing with buffer solution was found to be more successful and again indicated the value of a vigorous disturbance around the diaphragm.

Dripping acid continuously on to the top surface of the cathode diaphragm in an attempt to prevent precipitation of solid was fairly successful but the method was discarded as impracticable since contamination with alumina was rather heavy.

(vi) Use of ammonium chloride solution.

As an alternative to the use of sulphuric acid, it was decided to find the effect of suspending the mixed carbonates in ammonium chloride solution by which means it was hoped that a complex ion might be formed involving calcium which might then have a negative overall charge.

The/

The amounts of calcium and magnesium migrating to the cathode were small but it was found possible to cause more magnesium than calcium to migrate, bearing out the theory of complex formation. It was necessary to allow a period to elapse before commencing electrodialysis so that the complex formation had time to take place.

The use of stronger ammonium chloride caused more calcium than magnesium to be transferred to the cathode section and it is suggested that at the higher currents prevailing the complex ion may be broken up, releasing the calcium.

A test using calcium carbonate and magnesium oxide to simulate a half-calcined mixture gave very slightly more magnesium transferred than in the corresponding test but with the mixed carbonates, possibly due to a slightly greater solubility effect.

This method, although poor from the practical viewpoint of amounts transferred, was successful in that it was shown to be possible to reverse the normal ratio of calcium to magnesium migrating.

(vii) Use of carbon dioxide gas.

Passing a stream of carbon dioxide gas through a suspension of the mixed carbonates of calcium and magnesium should cause solution of the latter in the form of bicarbonate. This/

This method seemed feasible since it would give only the desired ions in solution without the possibly harmful and, at any rate, wasteful presence of free hydrogen, sulphate, ammonium or chloride ions in solution as is the case when sulphuric acid or ammonium chloride is used as the chemical additive.

A first test (G1) showed that more magnesium than calcium could be caused to migrate, although the amounts were small.

A new design of apparatus, Cell III (Figure 4) was used with a view to testing the possibility of a concentric arrangement of the electrodes, an improved result being obtained (G2). The Cell was intended as a prototype of a cell basically similar, in that a concentric arrangement of electrodes and diaphragm was envisaged but in which constant circulation of the anode and cathode liquids would be possible. It was hoped that this circulation would improve the migration rate by causing a disturbance of the liquid around the diaphragm, thus helping to remove any film of precipitated solid which might tend to form.

Before this apparatus was tested, however, it was decided that the use of carbon dioxide made possible the employment of cellulosic diaphragms which, it will be remembered, were found unsuitable for use with acid.

Tests/

Tests were therefore made in a glass cell (Figure 5) using cellulosic diaphragms (G3 - G5) and, for the first time, Duror dolomite was used.

The results indicated that it was necessary that the dolomite be half-calcined if the separation was to be successful. It was further shown that a second treatment allowed further separation to be achieved.

The fact that migration of calcium and magnesium occurred substantiates the theory, stated earlier, that when acid was used hydrogen ions migrated through the diaphragm to the complete, or almost complete exclusion of calcium and magnesium ions.

(viii) Use of circulation of anode and cathode liquids.

For the sake of completeness, tests were made using Cell V (Figure 6) with sulphuric acid, ammonium chloride and carbon dioxide as the chemical additives, half-calcined Duror dolomite being used in all these tests.

It was found that more magnesium than calcium migrated to the cathode in each case.

In accordance with previous work, the final test, using carbon dioxide, gave an excellent separation and the amount transferred was by far the greatest achieved in any test, confirming the belief that vigorous circulation would assist in the breakdown of precipitated films of solid on the diaphragm/

diaphragm.

It may be concluded, therefore, that the separation of magnesium from calcium, as they occur in dolomite, can be achieved electrodialytically.

The following conditions must be observed:

1. The dolomite must be calcined at a temperature which will cause conversion of the magnesium carbonate to magnesium oxide, leaving the calcium carbonate unchanged.

2. Electrodialysis must be carried out in a cell in which circulation of both the anode and cathode liquids can be made.

3. A buffer solution must be used in the cathode chamber to prevent that section from becoming strongly alkaline.

4. Diaphragms should, preferably, be of porous earthenware since Cellophane, although otherwise suitable, may not be strong enough to withstand the force of the circulating liquids.

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EXPERIMENTAL SECTION

PART I - INORGANIC

B. ELECTRODEPOSITION.

INVESTIGATION OF VARIABLES AFFECTING THE ELECTRODEPOSITION OF CALCIUM AND MAGNESIUM CARBONATES.

General.

Previous work on electrodeposition, as stated in a previous section (p. 49), has been mainly concerned with the formation of insulating coatings of inorganic materials on wires, tubes etc., for use in electrical work, and the deposition of coatings of rubber. Purification of clays by electrodeposition has also been investigated.

In the present work it was hoped to find applications of electrodeposition for the separation of calcium and magnesium in dolomite or, more feasibly, the removal of acid-insoluble material.

Previous Work.

The electrodeposition of powdered inorganic materials from suspension in organic liquids has been described by Hamaker,(146) who obtained deposits of barium carbonate, strontium carbonate, magnesium carbonate, magnesium oxide, aluminium oxide and calcium fluoride from suspension in methyl alcohol, ethyl alcohol, acetone and mixtures of these. He derived an expression relating the amount of deposit to the concentration, the electrical field, the electrode surface, the time and a constant dependent on the chemical constitution of the suspension. A rapid decrease in current was observed in some cases while deposition was proceeding, which he attributed to strong polarisation in the coating. Irregular results/

results were obtained when low concentrations, low voltages and short times of deposition were employed.

Hamaker and Verwey (142) have discussed the role of forces between particles in electrodeposition, stating that a stable suspension is necessary for the formation of a deposit and drawing a parallel between deposition obtained electrically and that obtained by sedimentation. They examined deposition under conditions where no energy minimum existed in the charge/distance of separation curve for the particles and showed that deposition was still possible. It was pointed out that deposits could be obtained which had a high mechanical strength while others might be very fluid in nature.

Hamaker (147) concluded that deposit-formation would not be greatly influenced by particle size since the forces exerted on the particle by the electrical field vary similarly to the forces acting between the particles.

Benjamin and Osborn (145) described the electrodeposition of oxide coatings using alkaline earth carbonates and alumina deposited on nickel or tungsten wire. Deposits of the carbonates were obtained from methyl alcohol and acetone but not from ethyl alcohol, propyl alcohol, butyl alcohol or amyl alcohol. Deposition from aqueous suspension was disturbed by gas formation at the electrodes. They reported an apparent polarising action with the carbonates but not with alumina. The addition of small amounts of water/

water, acid or alkali had little or no effect but larger quantities of acid or alkali inhibited the deposition. Details were given of the use of ethylene glycol to increase the viscosity of the suspending medium and of nitrocellulose as a binder.

Hill, Lovering and Rees (149) examined, theoretically and experimentally, the deposition of materials from non-aqueous media, taking into account the mutual interaction of the particles. They used a double carbonate of barium and strontium and determined the yield for various concentrations of suspension and at various potential differences. When high polymers were dispersed in the suspending medium a "critical voltage" appeared. They also found a critical time at which deposition set in and determined its dependence on applied potential and cathode radius. The critical voltage was thought to be due to a sudden change in electrokinetic properties caused by the introduction of the resin into the double layer. These authors stated that on no occasion did they observe any decrease in current during deposition, unless sufficient water was present to cause obvious gas evolution and they agree, therefore, with Hamaker's conclusions that such a drop is due to polarisation, attributing the results of Benjamin and Osborn to the presence of excessive moisture derived either from the suspending medium or from the suspended material.

Apparatus.

The apparatus used is shown in Figures 7 and 8, the electrical circuit being that shown in Figure 10.

Materials.

The materials used were:

Calcium carbonate (Analar); light magnesium carbonate (B.P.); heavy magnesium carbonate; magnesium hydroxide (Analar); calcium hydroxide (Analar); two samples of dolomite from Duror, Argyllshire and from Kishorn, Ross and Cromarty; half-calcined Duror dolomite; and dead-burnt Duror dolomite.

EXPERIMENTAL.

PRELIMINARY TESTS.

The apparatus used was that shown in Figure 7. Suspensions of calcium carbonate, light magnesium carbonate and dolomite were prepared in methanol and electrodeposition attempted. Deposits were obtained with all three, magnesium carbonate being the most coherent and calcium carbonate the least. It was noted that the currents obtained during deposition of calcium carbonate were considerably heavier (ca. ten times) than those with magnesium carbonate. An improved apparatus (Figure 8) was designed and used for all further tests.

Initial tests made during suspensions of calcium carbonate in ethyl alcohol gave very erratic results, high currents being obtained and electrolysis occurring. Deposits were very weak and tended to slip off the cathode during and after deposition.

For a systematic investigation of the variables affecting the process, therefore, ethanol was used as the ? m suspending medium. The currents obtained were lower, no electrolytic disturbances occurred and deposits were more coherent.

Experimental Procedure.

The method adopted was to make up the suspension in

a/

a suitable beaker, and immerse the electrode assembly to a fixed depth, supported on the rim of the vessel by wooden struts. Electrodeposition was then carried out for a given time, readings of the applied potential and current being taken. The electrode assembly was lifted from the suspension, the rubber collar supporting the cathode removed, and the rod pushed clear of the anode cylinder. The deposit was now removed from the rod, placed in a previously weighed filter paper, dried in an electric oven and weighed.

The reproducibility of results obtainable using this method was of the order of 2 per cent.

Experimental Results.

The results obtained are shown in Tables XII - XX and in Figures 13 - 20.

The following abbreviations are used:

MAG. CARB.	light magnesium carbonate.
HVY. MAG. CARB.	heavy magnesium carbonate.
CAL. CARB.	calcium carbonate.
MAG. HYD.	magnesium hydroxide.
CAL. HYD.	calcium hydroxide.
DUR. DOL.	Duror Dolomite.
KIS. DOL.	Kishorn dolomite.
HCD.	Half-calcined Duror dolomite.
DBD.	Dead-burnt Duror dolomite.

The/

The standard conditions of experiment adopted were:

Using calcium carbonate - 50g. suspended in 500 ml. ethyl alcohol. Potential of 150 v. applied for 30 seconds at room temperature. Length of electrode immersed 1 in.

Using magnesium carbonate (light) - 20g. suspended in 500 ml. ethyl alcohol. Potential of 150 v. applied for 30 seconds at room temperature. Length of electrode immersed $\frac{3}{4}$ in.

Effect of presence of water.

Calcium carbonate only was used. Conditions were standard except that the suspending media used were methyl alcohol, methyl alcohol containing 2% water, ethyl alcohol, and ethyl alcohol containing 2% water. The results of a series of tests in which the applied potential was varied are given in Table XVII and in Figure 17 from which it may be observed that the presence of water has no apparent effect. When 10-20% water was present the amount of deposit tended to decrease and was rather wet.

Effect of presence of acid.

Calcium carbonate only was used for this test under standard conditions of concentration in ethyl alcohol, varying amounts of sulphuric acid being added to the suspension. A potential of 100 volts was applied for 30 seconds. The addition of a small amount of dilute acid showed no effect but a larger quantity/

quantity inhibited deposition completely.

Effect of purity of suspending medium.

Calcium carbonate was used for this series of tests in which standard conditions were employed, apart from the suspending media, which were absolute methyl alcohol, commercial methyl alcohol (two samples), commercial methyl alcohol with 2% water added, absolute ethyl alcohol, commercial ethyl alcohol and commercial ethyl alcohol with 2% water added. In each case, a series of tests were made at different applied potentials. The results are shown in Table XVII and in Figure 17. It will be seen that absolute methyl alcohol gave the greatest amount of deposit, one sample of commercial methyl alcohol and the same sample with 2% water giving somewhat less. The other sample of commercial methyl alcohol gave completely erratic results. No significant differences were observed in the results obtained with the ethyl alcohol.

Effect of different suspending media.

Both carbonates were used in this series of tests which was made in a smaller container. 15 gm. of calcium carbonate and 5 gm. of light magnesium carbonate were used each in 150 ml. of liquid. A potential of 240 volts was applied for 30 seconds. The liquids were all of Analar quality, except *n*-propyl alcohol, which was of B.P. standard, and *cyclo*hexanone, which was re-distilled. The results are shown/

shown in Table XVIII, together with the values of the dielectric constant, and in Figure 18 which shows the amount of deposit plotted against the dielectric constant of the liquid concerned. With two exceptions the amount of deposit increased with increasing dielectric constant, the exceptions being acetone and nitrobenzene.

Effect of concentration.

Standard conditions were used, but methyl alcohol was used as suspending medium for all the materials except calcium and light magnesium carbonate. The concentration of solid in suspension was increased throughout the series. The results are given in Table XIX. Calcium carbonate (Figure 19) and two samples of dolomite all gave a linear relationship, but with light and heavy magnesium carbonates, and calcium and magnesium hydroxide, increasing concentration caused a very rapid increase in the amount of deposit.

Using samples of Duror dolomite, half-calcined Duror dolomite and dead-burnt Duror dolomite (Figure 20), a rapid increase was found initially, becoming linear at higher concentrations. The actual amounts of deposit obtained at equal concentrations increased in the order - dolomite, half-calcined dolomite, dead-burnt dolomite.

Effect of Fineness of Material.

Two samples each of calcium carbonate and heavy

magnesium/

magnesium carbonate were used, one without grinding and the other after grinding for 2 hours in a pebble mill. Deposition was carried out for 30 seconds at 240 V. using a concentration of 15g. in 150 ml. of methyl alcohol. The results (Table XX) showed no difference with the calcium carbonate but a considerable increase in the amount of deposit with the ground magnesium carbonate as compared with the unground material.

Additional information about the materials used was obtained from infra-red absorption curves and from photomicrographs.

The infra-red absorption spectra were recorded using a double-beam spectrophotometer and will be found in Appendix I (Figures 23 and 24).

The photomicrographs were made using a Vickers projection microscope and are given in Appendix II. (Plates 5 - 16).

The results obtained are presented in Table XXI.

DISCUSSION OF RESULTS.

The observed linear relationships between the amount of deposit on the one hand and time, concentration (in some cases), applied potential, and electrode surface on the other, are in agreement with the results of Hamaker (146) and of Biguenet/.

Biguenet and Mano (150). The latter also reported a decrease in the amount of deposit with increasing temperature, which was not observed in the present investigation.

The initial portions of the graphs, between the origin and the first experimental point are, in some cases, not a smooth continuation of the rest of the curve and this is attributed to the unique conditions existing at this stage. The initial deposit is formed on the surface of the cathode rod while material deposited later builds up on the previously deposited coating. It follows that, in the lower region of the curve where the weight of deposit is small, the former effect will be relatively large.

The fact that many of the curves depart from a linear relationship is thought to be due to the quantities dealt with. Very large deposits were obtained, and the departures may well have been due to deposited material breaking off under its own weight. The point at which this occurs appears to vary considerably, possibly because the mechanical strength of the deposit is dependent, to some extent, on the experimental conditions. Previous experiments on the other hand, have been on a very much smaller scale, where deposits were not sufficiently heavy to cause any difficulties.

The results obtained when water and acid were added to the suspending medium agree with those published by

Benjamin/

Benjamin and Osborn (145), while the very erratic results obtained with a particular sample of commercial methyl alcohol (Figure 17) show the advisability of ensuring the purity of the suspending medium.

The exceptional behaviour of acetone is not in agreement with previously published work, Hamaker (146), Benjamin and Osborn (145), and Biguenet and Mano (150) reporting normal deposit formation. An obvious difference between acetone and the series of alcohols used is the absence of the hydroxyl group in the former, the enol form in acetone being vanishingly small under the experimental conditions. To check this point, *cyclo*hexanone was used as suspending medium, since it is known to have about 12% enol form under normal conditions (213). The results indicate (Figure 18) that the presence of the hydroxyl group in the suspending medium is necessary for successful deposition, while with hydroxyl groups in the suspended solid, deposition is enhanced and unusual concentration effects are observed. (Figure 19). The possibility of some form of hydrogen bonding involving hydroxyl groups must be considered, a factor which is not possible with acetone suspensions.

The rapid increase of deposit with increasing concentration is also unexpected. The particle size examination showed that this was certainly not a controlling factor and it was/

was observed that these abnormal results were obtained with solids which contained hydroxyl groups and not with those which had no hydroxyl groups. The suspensions in which the effect was noted were observed to be almost pastelike at the higher concentrations and Hill, Lovering and Rees (149) have pointed out the probability of abnormal results under such conditions due to interaction of the suspended particles. Considering this effect in conjunction with that noted with acetone, it is tentatively suggested that hydrogen bonding may play an important part in determining the interaction of particles in suspension.

The current almost always decreased during deposition, by an amount showing a general parallelism with the amount and firmness of the deposit. If the deposit was wet, the drop in current was less than if the deposit was relatively non-porous. Even when every precaution was taken to ensure the absence of water from both the suspended solid and the suspending medium, the current still decreased during deposition. It would seem, therefore, that the effect is due to the insulating effect of the coating of inorganic material on the cathode surface and not to polarisation.

Currents were always higher with calcium carbonate than with magnesium carbonate when suspended in methyl alcohol and at higher concentrations were so large that excessive heating/

heating was unavoidable, thus preventing any examination of the effect of very high concentrations of this material. It would appear that some reaction must take place between the calcium carbonate and methyl alcohol giving rise to ionisation. It proved impossible to work at high concentrations of calcium carbonate in ethyl alcohol, owing to the extreme weakness of the structure of the deposit, which broke away from the electrode under its own weight as soon as the applied potential was removed. It was, therefore, not possible to find out whether calcium carbonate could be made to exhibit the abnormal increase with concentration observed with the basic magnesium carbonates.

The results obtained using Duror dolomite and the same material after partial or complete calcination show a different type of increase with concentration, the effect being most apparent at lower values. It was also seen that the amount of deposit obtained at equal concentrations was greater with dead-burnt dolomite than with the half-calcined material while that with the half-calcine was greater than the original dolomite. It is thought, therefore, that the controlling factor here is the closer packing of the molecules made possible by the removal of some of the carbonate in one case and all of it in the other. The half-calcined and dead-burnt dolomite were observed to have become amorphous, whereas the/

the original dolomite was crystalline and the strength of the deposit may have been increased as a result of better packing and sintering of the deposit. This view is supported since it was observed that deposits of calcined dolomite were much more adherent and coherent.

Reference to Plates 5, 6, 8 and 9 (Appendix II), will show that the grinding of calcium carbonate was not nearly so effective as with heavy magnesium carbonate and this explains why an increased deposit was obtained with one and not with the other. The reason for the increase with magnesium carbonate may be closer packing of the finer material.

TABLE XII.

Variable.	Material.	Figure.	Remarks.
Temp.	Ca Carbonate	13	Tendency for amount of deposit to increase with increase in temp.
(12-32°C)	Lt. Mg. carb.	13	Little or no effect.
App. Pot.	Ca carbonate	14	Linear increase in amount of deposit with increase in applied potential.
(50-230V)	Lt. Mg. carb.	14	Linear increase initially, falling away latterly.
Electrode Surface	Ca carbonate	15	Linear increase in amount of deposit with increase in amount of electrode surface.
(0.6-3.5 in. length)	Lt. Mg. carb.	15	Linear increase in amount of deposit with increasing electrode surface.
Time.	Ca carbonate	16	Linear increase initially with increase of time, falling away latterly.
(30-180 secs.)	Lt. Mg. carb.	16	Linear increase in amount of deposit with increase of time initially, falling away latterly.

TABLE XIII.

Effect of Temperature.

Calcium Carbonate

Temp. (°C.)	Current Drop(ma)	Weight of Deposit (Gm.)
12	0	0.30
16	5	0.33
20	5	0.36
24	5	0.38
28	5	0.39
32	5	0.43

Light Magnesium Carbonate

Temp. (°C.)	Current Drop (ma)	Weight of Deposit (Gm)
12	0	0.28
17	0	0.27
20	0	0.26
24	0	0.25
27	0	0.26
31	0	0.26

TABLE XIV.

Effect of Applied Potential.

Calcium Carbonate

Applied Potential (Volts)	Current Drop (ma.)	Weight of Deposit (gm.)
50	0	0.06
100	0	0.24
150	5	0.40
200	10	0.55
230	15	0.69

Light Magnesium Carbonate

Applied Potential (Volts)	Current Drop (ma.)	Weight of Deposit (gm.)
50	0	0.04
100	0	0.12
150	0	0.19
200	0	0.22
230	5	0.25

TABLE XV.

Effect of Electrode Surface.

Calcium Carbonate.

Length of Electrode immersed (ins.)	Current Drop (ma.)	Weight of Deposit (gm.)
0.6	0	0.16
1.2	5	0.49
1.8	10	0.83
2.6	15	1.23
3.2	20	1.71

Light Magnesium Carbonate

Length of Electrode immersed (ins.)	Current Drop (ma.)	Weight of Deposit (gm.)
0.8	0	0.31
1.7	0	0.62
2.6	5	0.96
3.5	15	1.24

TABLE XVI.

Effect of Time.

Calcium Carbonate

Duration of Test (secs.)	Current Drop (ma.)	Weight of Deposit (g.)
30	5	0.35
60	10	0.71
90	10	1.03
120	10	1.28
150	10	1.47
180	15	1.68

Light Magnesium Carbonate

Duration of Test(secs.)	Current Drop (ma.)	Weight of Deposit (g.)
30	0	0.27
60	0	0.39
90	0	0.44
120	5	0.51
150	5	0.60
180	8	0.61

TABLE XVII.

Effect of Purity of Suspending Medium.

Applied Potential (Volts)	Weight of Deposit when Suspended in						
	Abs. Methyl Alcohol	Comm. Methyl Alcohol I	Comm. Methyl Alcohol II	Comm. Methyl Alcohol & water	Abs. Ethyl Alcohol	Comm. Ethyl Alcohol	Comm. Ethyl Alcohol & water
50	0.58	0.30	0.08	0.30	0.10	0.06	0.15
100	1.24	0.84	0.09	0.89	0.23	0.20	0.29
150	1.97	1.25	0.16	1.77	0.35	0.36	0.39
250	2.72	1.95	0.32	1.95	0.48	0.45	0.60
230	2.69	2.30	0.35	2.30	0.58	0.55	0.66

Table XVIII.

Effect of Suspending Medium.

Suspending Medium	Dielectric Constant	Weight of Deposit(g) of Calcium Carb.	Magnesium Carb.
Methyl Alcohol	33.7	1.11	0.54
Ethyl Alcohol	25.7	0.40	0.22
n-Propyl Alcohol	21.8	0.30	0.20
n-Butyl Alcohol	17.8	0.12	0.12
n-Amyl Alcohol	15.8	0.08	0.07
Acetone	21.3	0.01	0.04
Ethyl acetate	6.4	0.01	0.02
Nitrobenzene	36.1	-	-
Cyclohexanone	15.0	-	0.07

TABLE XIX.

Effect of Concentration.

			Weight of Deposit (g.) given by						
Conc. of Suspensoid (g./cc).	Cal. Carb.	Mag. Carb.	Hvy. Mag. Carb.	Cal. Hyd.	Mag. Hyd.	Kis. Dol.	Dur. Dol.	HCD	DBD
0.04		0.24							
0.08		0.72							
0.10	0.26		0.94	1.50	0.74	1.06	0.58	0.79	0.50
0.12		2.01							
0.16		6.22							
0.20	0.51		1.26	3.87	2.10	3.27	1.15	1.28	1.28
0.30	0.75		2.27	6.53	3.85	4.91	1.56	2.08	3.08
0.40	1.01		4.35	10.32	6.13	6.37	2.19	3.28	
0.50	1.40		12.51	16.38	13.45	7.43	2.72	4.49	

TABLE XX.

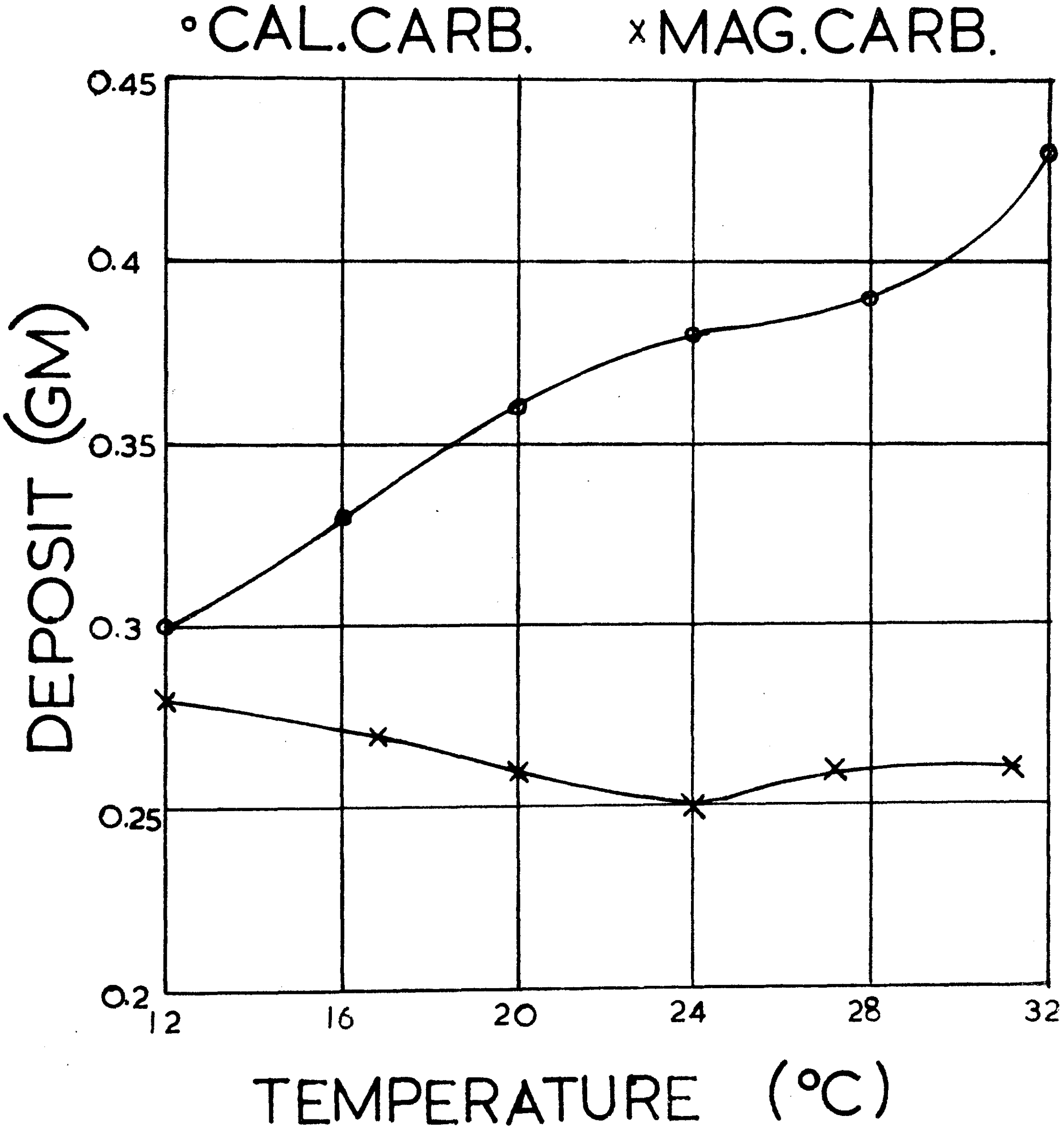
Effect of Fineness of Material.

Material	Current Drop (ma.)	Weight of Deposit(g.)
Calcium Carbonate	50	1.03
Calcium Carbonate (Ground)	55	1.00
Heavy Magnesium Carbonate	70	0.68
Heavy Magnesium Carbonate(Ground)	100	2.45

TABLE XXI.

Data from Infra-Red Spectra and Photomicrographs.

Material Examined	Particle Size (Microns) from Photomicrographs	Hydroxyl Group present (+) or Absent (-) from I. R. Spectra
Calcium Carbonate.	Fairly Uniform. About 10.	-
Calcium Carbonate (Ground).	Wide Range. Mainly 5-10.	-
Heavy Magnesium Carbonate.	Fairly Uniform. About 10-15.	+
Heavy Magnesium Carbonate. (Ground)	Fairly Uniform. 1-2.	+
Light Magnesium Carbonate.	Fairly Uniform. 1 or less.	+
Calcium Hydroxide.	Mainly 3-5	+
Magnesium Hydroxide.	Mainly 1-3.	+
Kishorn Dolomite.	Mainly 2-4 and 8-10.	-
Duror Dolomite.	Mainly 2-3.	-
Half-calcined Duror Dolomite.	Mainly 5-10.	-
Dead-Burnt Duror Dolomite.	Mainly 3-5.	-
Acetone.	-	-
Cyclohexanone.	-	+



○ CAL.CARB.
× MAG.CARB.
DEPOSIT (GM)
0.45
0.4
0.35
0.3
0.25
0.2
12
16
20
24
28
32
TEMPERATURE (°C)

FIGURE 13

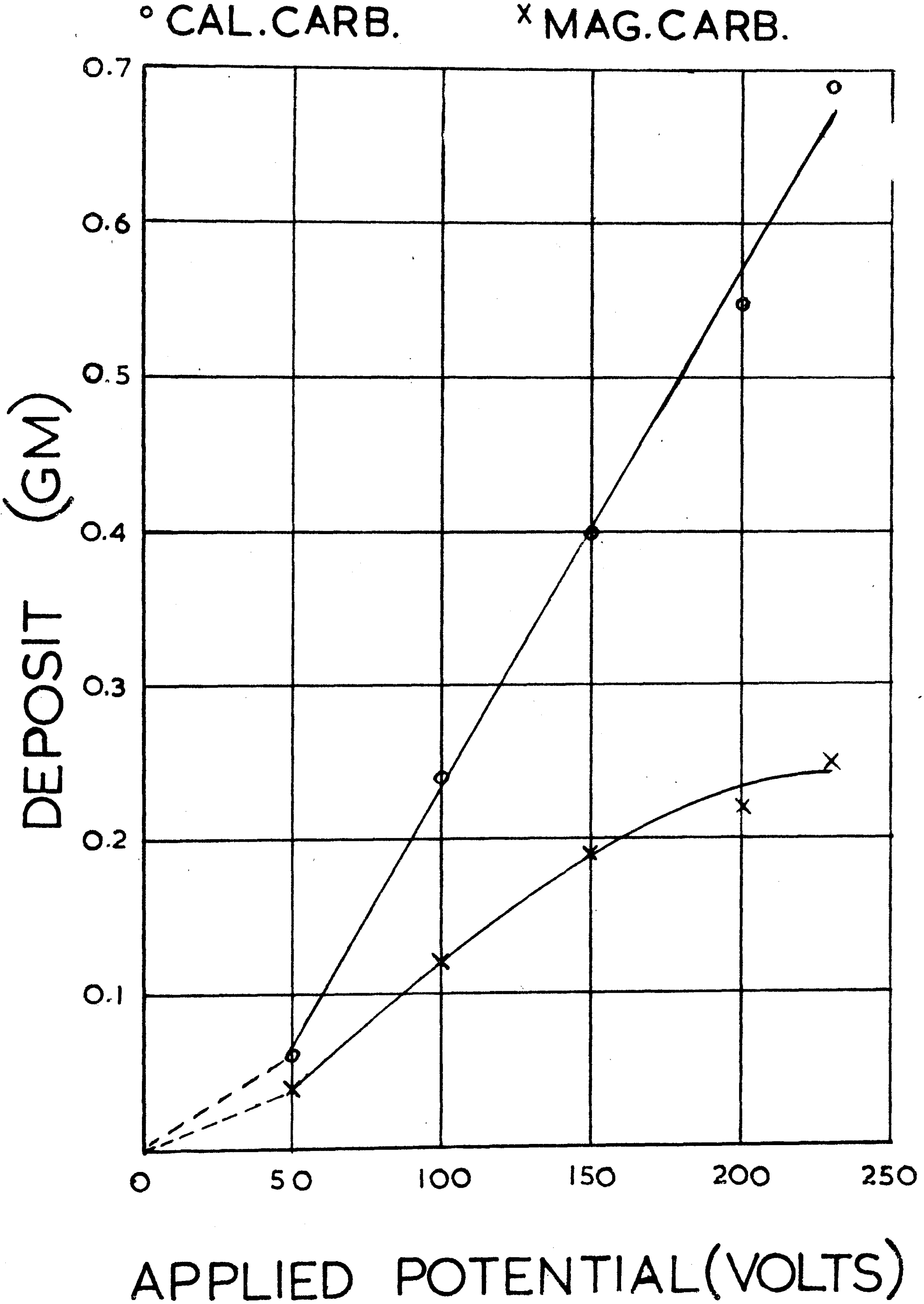

° CAL.CARB.
x MAG.CARB.
DEPOSIT (GM)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
250
APPLIED POTENTIAL(VOLTS)

FIGURE 14

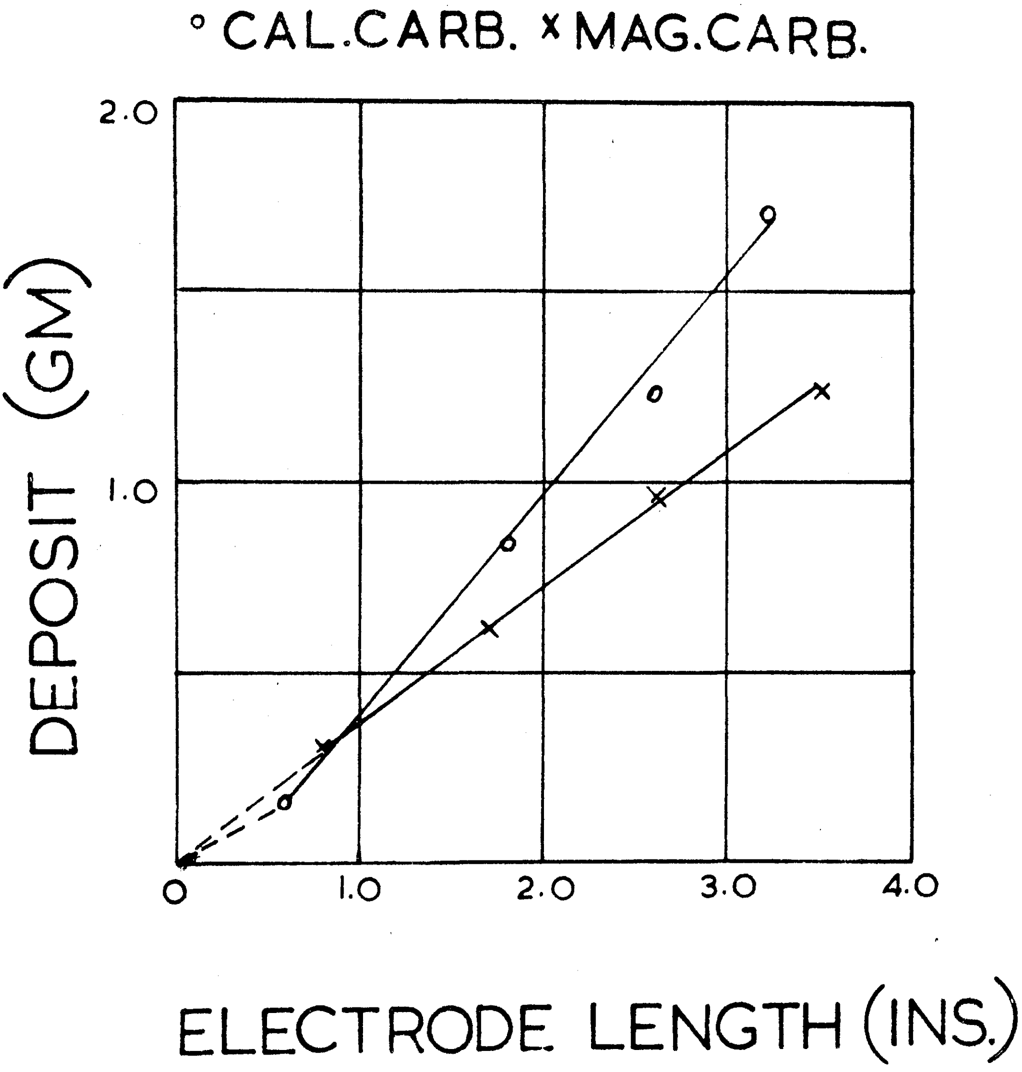

° CAL.CARB. × MAG.CARB.
2.0
1.0
0
1.0
2.0
3.0
4.0
DEPOSIT (GM)
ELECTRODE LENGTH (INS.)

FIGURE 15

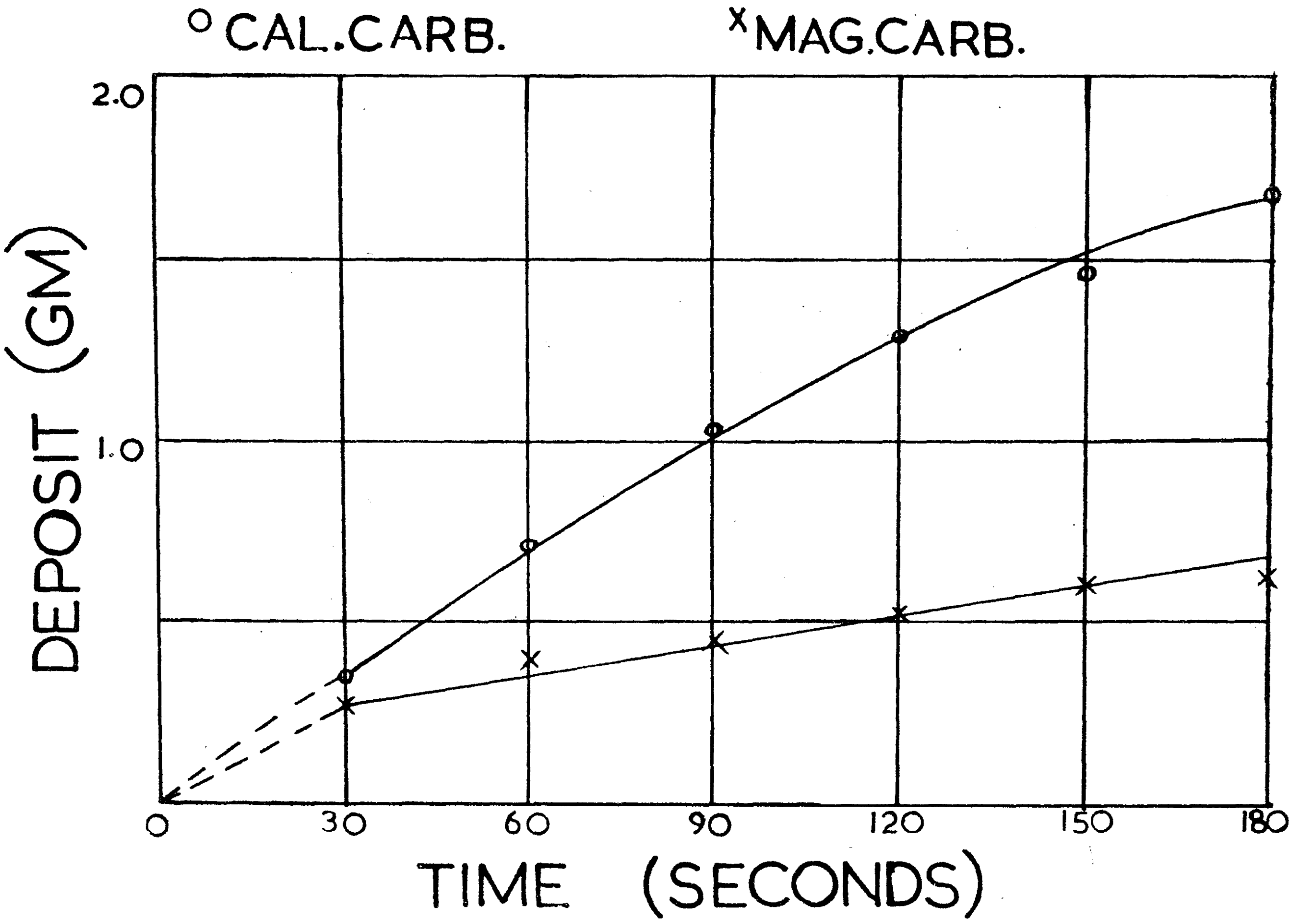

○ CAL.CARB.
× MAG.CARB.
2.0
1.0
DEPOSIT (GM)
0
30
60
90
120
150
180
TIME (SECONDS)

FIGURE 16

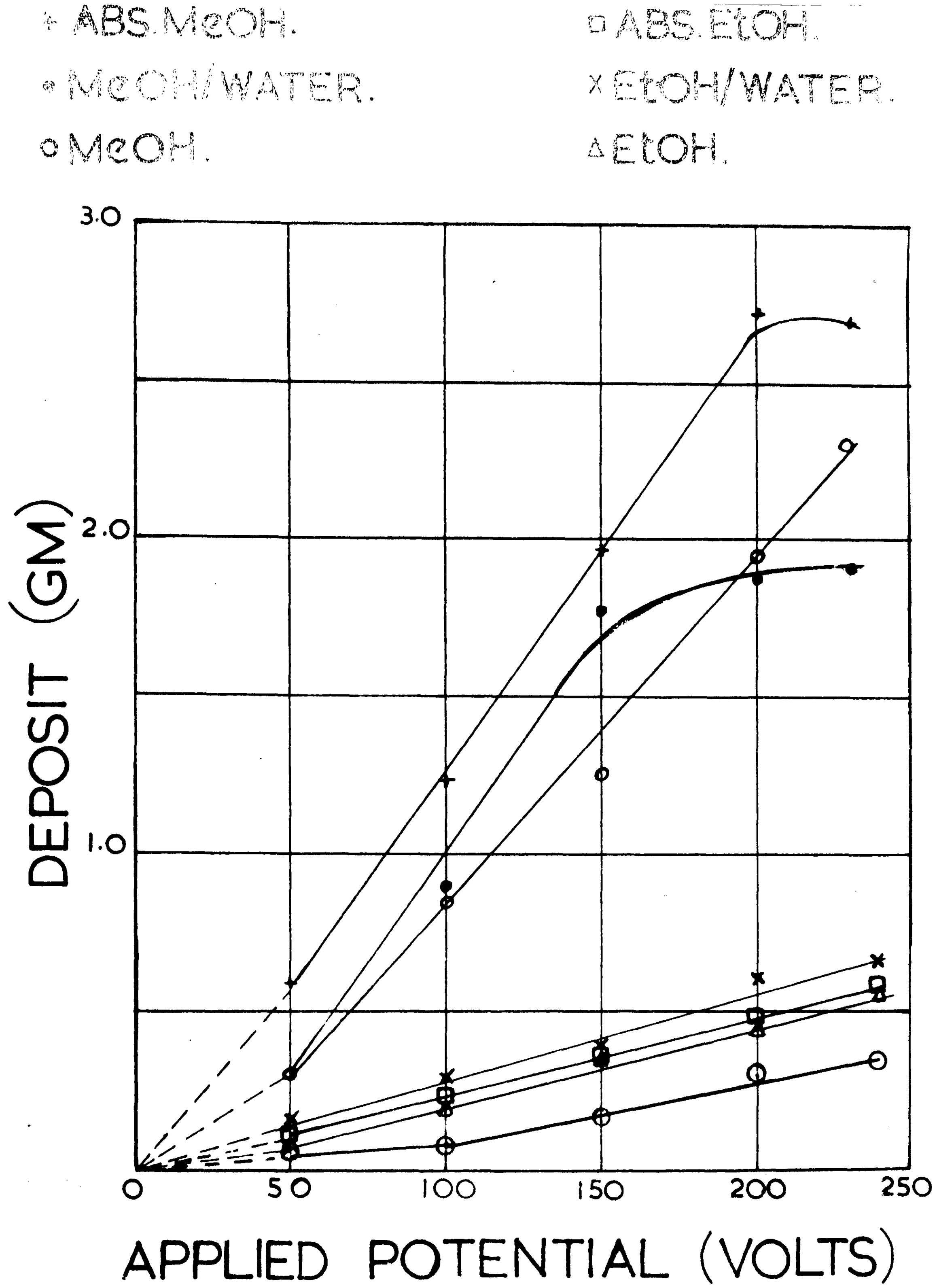

+ ABS.MeOH.
□ ABS.EtOH.
● MeOH/WATER.
× EtOH/WATER.
○ MeOH.
△ EtOH.
3.0
2.0
1.0
DEPOSIT (GM)
0
50
100
150
200
250
APPLIED POTENTIAL (VOLTS)

FIGURE 17

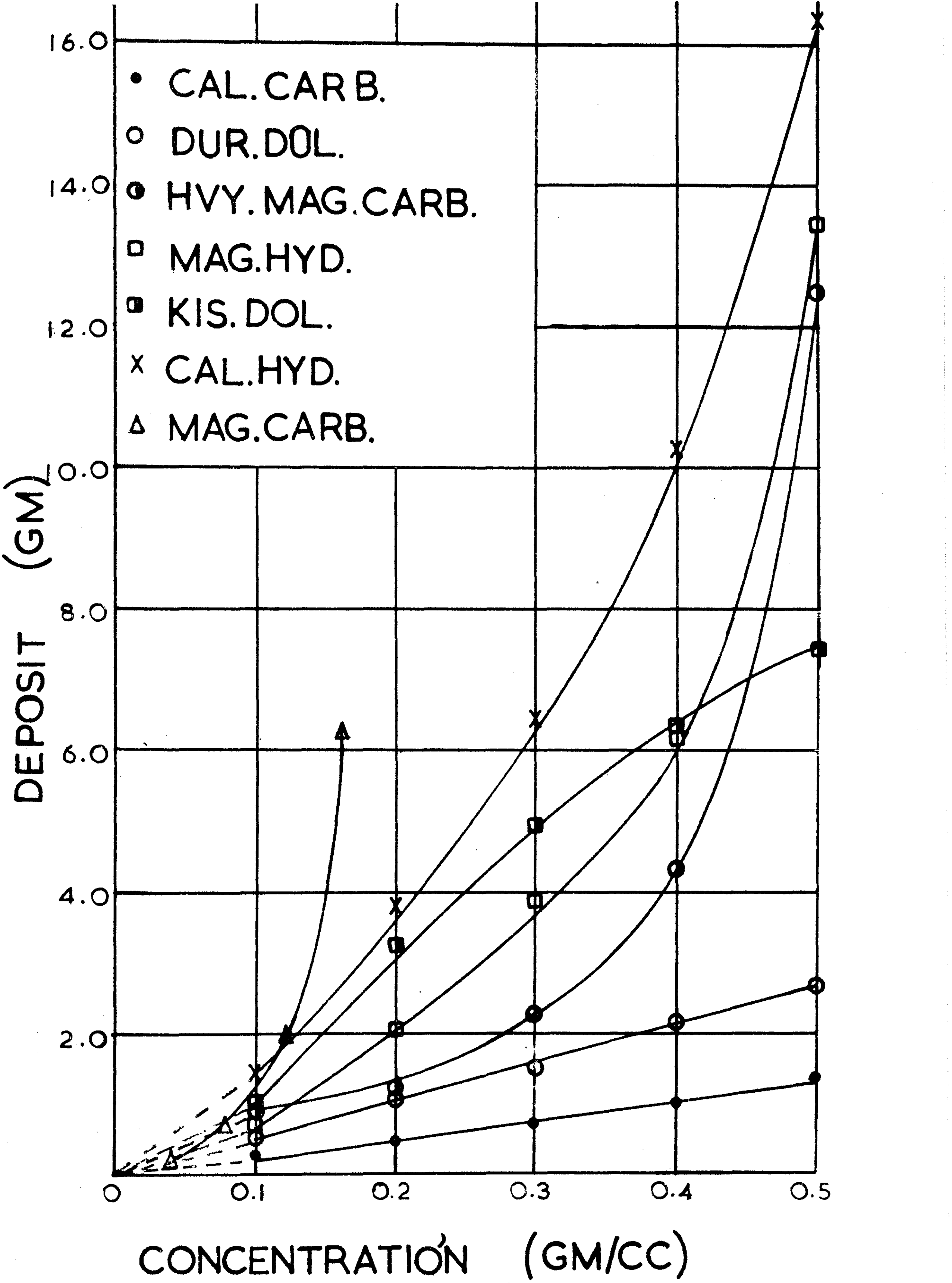

16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
0.1
0.2
0.3
0.4
0.5
DEPOSIT (GM)
CONCENTRATION (GM/CC)
● CAL. CARB.
○ DUR. DOL.
◐ HVY. MAG. CARB.
□ MAG. HYD.
▣ KIS. DOL.
X CAL. HYD.
△ MAG. CARB.

FIGURE 18

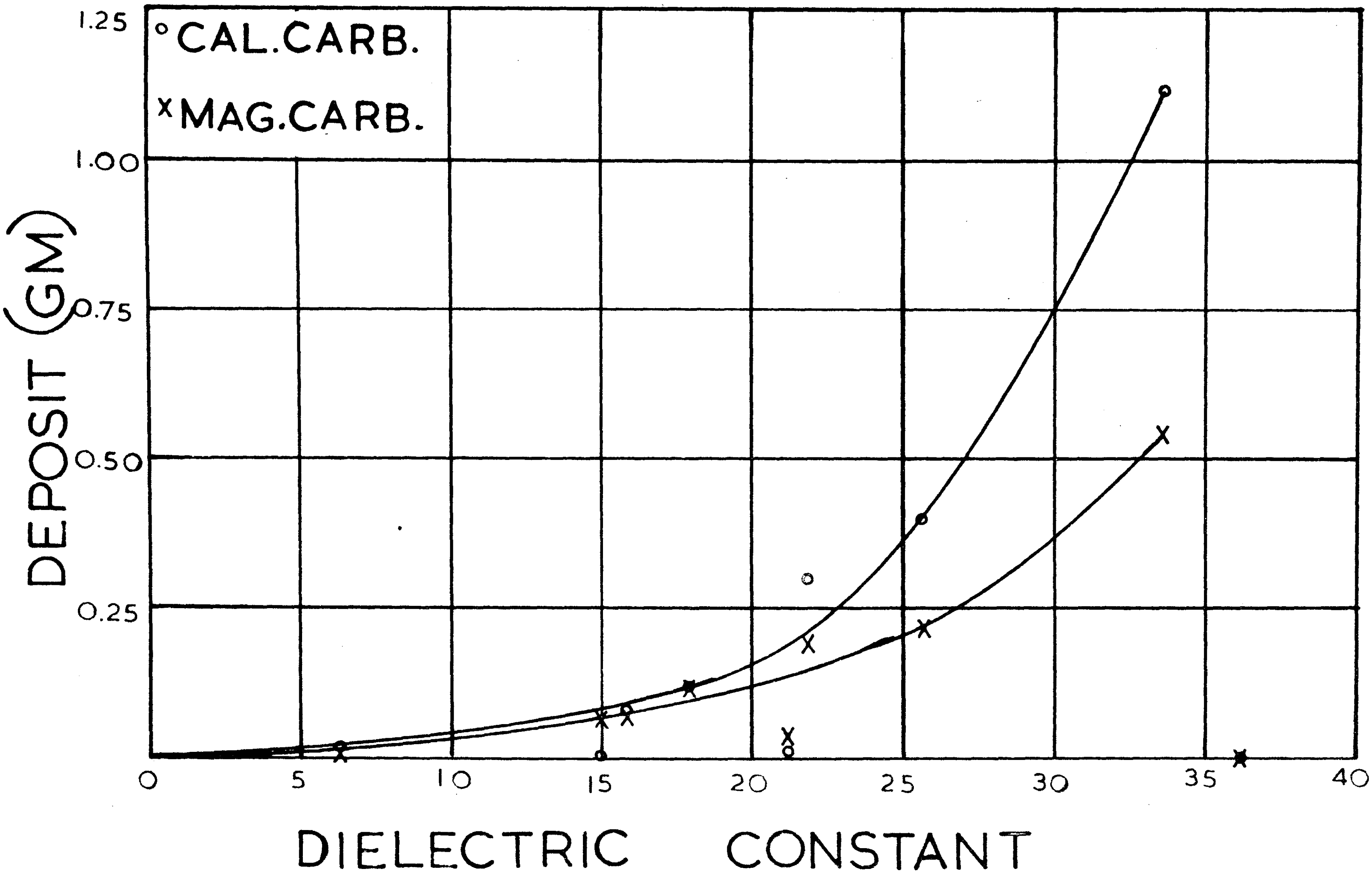

°CAL.CARB.
×MAG.CARB.
DEPOSIT (GM)
1.25
1.00
0.75
0.50
0.25
0
5
10
15
20
25
30
35
40
DIELECTRIC CONSTANT

FIGURE 19

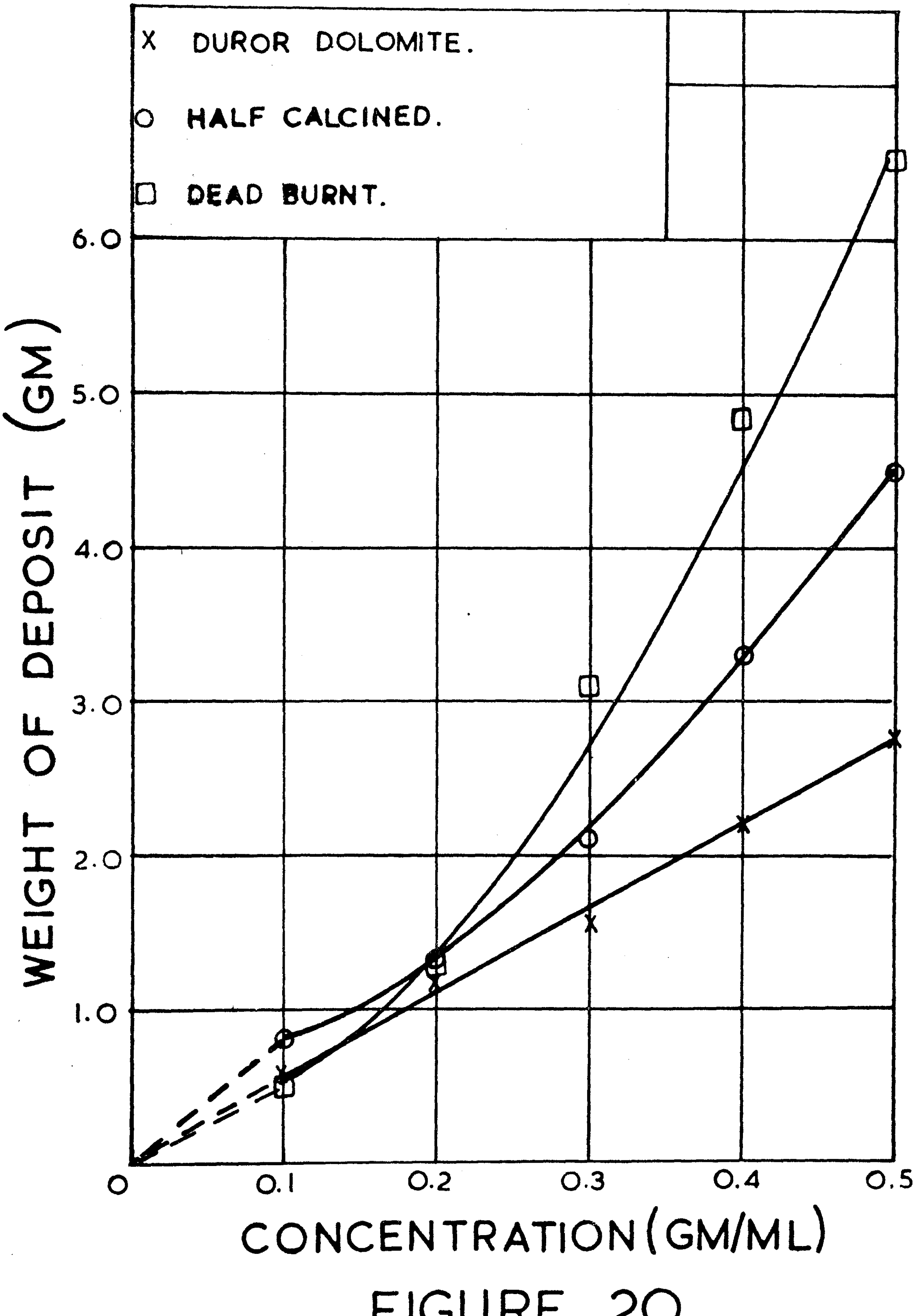

X DUROR DOLOMITE.
O HALF CALCINED.
□ DEAD BURNT.
WEIGHT OF DEPOSIT (GM)
6.0
5.0
4.0
3.0
2.0
1.0
0
0.1
0.2
0.3
0.4
0.5
CONCENTRATION (GM/ML)

FIGURE 20

EFFECT OF ELECTRODEPOSITION ON CONSTITUTION OF DOLOMITE.

Using the apparatus shown in Figure 8 and the same method as in the previous section, Duror dolomite and Kishorn dolomite were deposited electrically to determine whether or not the deposition changed the constitution of the minerals.

In both cases 30g. of dolomite were suspended in 150 ml. of methyl alcohol and a potential of 230 V. applied for 30 seconds.

Duror dolomite gave a deposit of 0.47 g. while 1.02 g. of Kishorn dolomite were deposited.

Analyses of the minerals before and after deposition are given in Table XXII.

It will be noted that except for a reduction in the acid-insoluble content, there is no real alteration in the minerals.

This would be expected, since a double-carbonate will deposit as such, there being no cause whatever for it to alter in any way.

TABLE XXII.

Analyses of Duror and Kishorn Dolomites before and after Electrodeposition.

Duror Dolomite Electro-Deposition	Constituent (%)			
	Acid. Insol.	R_2O_3.	CaO.	MgO.
Before	4.22	0.79	29.35	20.61
After	3.27	0.82	29.65	20.64

Kishorn Dolomite Electro-deposition	Constituent (%)			
	Acid. Insol.	R_2O_3.	CaO.	MgO.
Before	2.27	0.67	28.68	21.57
After	2.11	0.69	29.02	21.54

REDUCTION OF ACID-INSOLUBLE CONTENT OF DOLOMITE BY ELECTRODEPOSITION.

Introduction.

Dolomite is a soft rock but the acid-insoluble content, being mainly silica, is relatively hard. Grinding of the ore and sieving should, therefore, tend to segregate the acid-insoluble material in the coarser fractions of the mineral. This is an application of differential grinding as described by De Vaney (214).

Additionally, since silica carries a negative electrical charge and the carbonate portion a positive charge, separation by electrical means is a distinct possibility.

(a) Differential Grinding.

As a first step, a sample of Duror dolomite, containing 12% acid-insoluble material, was ground in a jaw-crusher and further reduced in size by passing it several times through a roller-crusher. The resultant material was mechanically sieved and each fraction analysed for acid-insoluble content using the method given earlier.

The results of the initial test are shown in Table XXIII, from which it can be seen that there is a considerable differential effect, the coarser material containing about 20% acid-insoluble and the finer material only about 4%.

Tests were made in which grinding was successively

less/

less severe. In the first test the dolomite was ground in the jaw-crusher and then passed five times through the roller-crusher, the rolls being set $\frac{1}{8}$" apart. In the second test the material from the jaw-crusher was passed twice through the roller-crusher, in the third once and, finally, not at all. The results are shown in Table XXIII.

It is obvious that crushing is too severe and the figure of 2.4% acid-insoluble content in the ex. 300 B.S.S. fraction is the minimum obtainable if the jaw-crusher is used as the primary grinding unit. The amount of material ground to this size is small, being only about 5% of the original weight.

In order to obtain greater efficiency, a test was made in which material which had been previously passed through the jaw-crusher and the roller-crusher, was ground in a porcelain ball-mill. Approximately 55% of the product passed a 200 mesh B.S.S. sieve but the acid-insoluble content of this material was 11.7%.

It was concluded, therefore, that a high throughput was incompatible with a low acid-insoluble content in the product.

(b) Electrodeposition.

Samples of Duror and Kishorn dolomites were taken, passing 200 but retained on 300 mesh B.S.S. The acid-insoluble contents of the samples were determined and found to be 4.22% for/

TABLE XXIII.

Acid-Insoluble Content of Duror Dolomite size-fractions after crushing.

Method of Crushing	Acid-insoluble content (%)				
	On 90	90/140	140/200	200/300	Ex 300
Passed through jaw-crusher and 5 times through roller-crusher with $\frac{1}{8}$" separation of rolls	19.8	19.2	12.8	4.22	4.35
Passed through jaw-crusher and twice through roller-crusher	-	-	-	5.5	2.6
Passed through jaw-crusher and once through roller-crusher	-	-	-	5.7	2.5
Passed through roller-crusher only	-	-	-	5.5	2.4

for the Duror and 2.34% for the Kishorn dolomite.

50g. of the Duror dolomite sample were suspended in 500 ml. of methyl alcohol (in Cell II, Figure 8), and a potential of 240 V. applied for 120 seconds. The amount of deposition was small and the process was repeated twice more, giving a total deposit of 2.34 g. with an acid-insoluble content of 2.74%. It was noted that the deposit was very wet in character and had poor mechanical strength.

A similar test was made using 50 g. of Kishorn dolomite suspended in 200 ml. of methyl alcohol. A potential of 240 V. was applied for 60 seconds and deposition made three times. The deposit which formed was very compact and rigid, having a total weight of about 15 g. The acid-insoluble content was found to be 2.15%.

From these tests it was deduced that the acid-insoluble content of the Duror dolomite must exist mainly as free silica, e.g., quartz, since there was a marked reduction on electrodeposition. Kishorn dolomite, on the other hand, was presumed to contain mainly combined silica, as the acid-insoluble content was only slightly reduced.

Since the amount of dolomite passing 200 mesh B.S.S. but retained on 300 mesh B.S.S. and containing only about 4% acid-insoluble obtained from a given sample was of the order of 5 - 10%, it is clear that if electrodeposition is to be completely/

completely successful the need for preliminary differential grinding must be avoided. To determine whether such a process could be avoided, two tests were made using dolomite of a much coarser nature and containing a high percentage of acid-insoluble material. In the first test, dolomite retained on a 90 mesh B.S.S. and having an acid-insoluble content of 18.8% was used, while in the second the 90/140 mesh B.S.S. fraction was used, the acid-insoluble content being 19.2%. By a single electro-deposition the acid-insoluble contents were reduced to 6.9% and 4.4% respectively. From this it was deduced that no preliminary differential grinding was necessary. Further, since the acid-insoluble content of the finer material had been reduced to a markedly greater extent, it seemed that the ideal material for use in such a process would be as fine as possible regardless of the initial acid-insoluble content.

The further reduction of acid-insoluble material was attempted with both dolomites by a series of tests in which previously deposited material was used to form the suspension in a further stage. The results of these tests are shown in Table XXIV and when graphed (Figure 21) give further evidence that the deductions regarding the nature of the acid-insoluble material are correct.

It was impossible to carry the process further with Duror dolomite since insufficient material was available from the third deposition to enable a fourth suspension of adequate concentration/

TABLE XXIV.

Reduction of Acid-Insoluble Content of Duror and Kishorn dolomites by electrodisposition.

Material	No. of deposition.	Acid-insoluble content (%)
Kishorn dolomite	0	2.34
	1	2.15
	2	2.01
Duror dolomite	0	4.22
	1	3.34
	2	2.30
	3	1.48

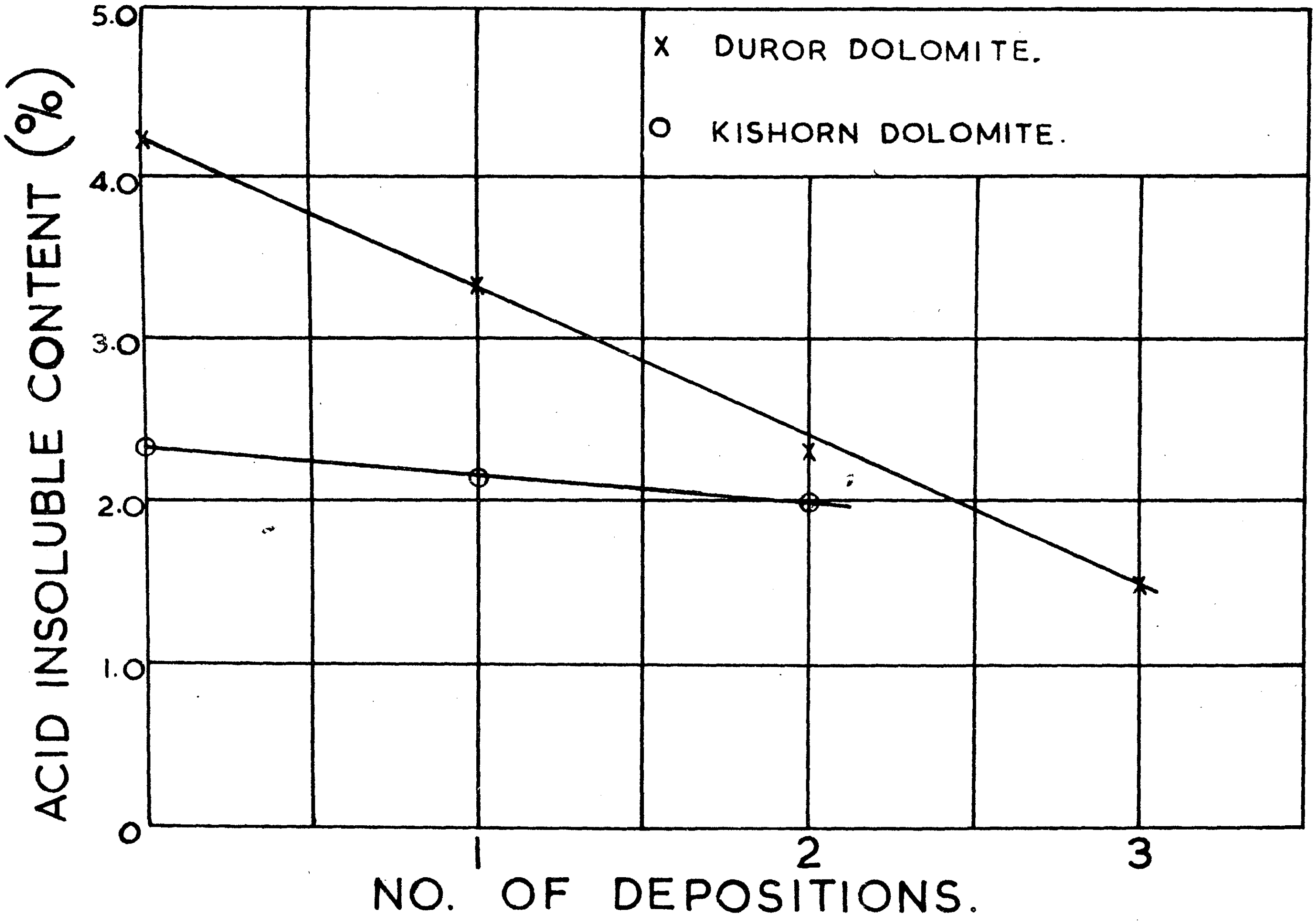

X DUROR DOLOMITE.
O KISHORN DOLOMITE.
ACID INSOLUBLE CONTENT (%)
5.0
4.0
3.0
2.0
1.0
0
1
2
3
NO. OF DEPOSITIONS.

FIGURE 21

concentration to be made.

Attempts to obtain the necessary quantities by commencing with a much higher concentration of dolomite were unsuccessful since, at these concentrations, the mechanical strength of the deposit was insufficient to allow of its removal, the entire deposit breaking away from the electrode immediately it was lifted from the suspension.

It had been noted (p.133) that half-calcined Duror dolomite gave a strongly adherent and coherent deposit, possibly due to the amorphous nature of the material. It seemed likely, therefore, that a multi-stage process would be more easily accomplished using it as the suspended solid.

The acid-insoluble content of the half-calcined dolomite was found to be 4.01%, this being reduced to 2.33% after one deposition.

Dead-burnt dolomite was not so suitable since the deposit, while coherent, was marked as if by gas formation causing a very uneven surface, making reproducibility of results uncertain. The acid-insoluble content of the dead-burnt dolomite was reduced from 5.45% to 3.24% after electrodeposition.

Accordingly, a multi-stage deposition process was carried out using half-calcined Duror dolomite, the results of this series of tests being given in Table XXV.

It/

TABLE XXV.

Reduction of Acid-Insoluble Content of Half-Calcined Duror Dolomite by Repeated Electrodeposition.

Stage No.	Conc. (g./ml. MeOH	No. of Depositions.	Total Weight of Deposit (g.)	Average Drop in Current (ma.)	Acid-Insoluble Content of Deposit.
1	150/300	10	90	300	3.12
2	85/175	10	33	100	2.25
3	30/100	14	8	30	1.34
4	6.5/25	4	1.7	15	0.86

It was found possible to complete a four-stage deposition, although at the last stage the suspension volume had to be reduced very considerably. The effect of repeated deposition of the material is shown in Figure 22, from which it may be seen that, after four depositions, the acid-insoluble content had been reduced from 4.04% to 0.86%.

The deposits were not nearly so firm as had been obtained with the first sample of half-calcined material and it is thought the endothermic reaction may have lowered the furnace temperature sufficienfly to prevent all of the dolomite being half-calcined.

Conclusions.

A material reduction in the acid-insoluble content of Duror dolomite was achieved by electrodeposition.

Differential grinding was also successfully applied but its application was limited since it was found impossible to obtain a large amount of the mineral with a low acid-insoluble content. If grinding was made more severe or prolonged to increase the amount of dolomite in the finer fraction, the acid-insoluble content of the fraction was increased, the harder material also being more greatly affected.

Electrodeposition of the coarser fractions, however, showed that preliminary differential grinding was unnecessary, since/

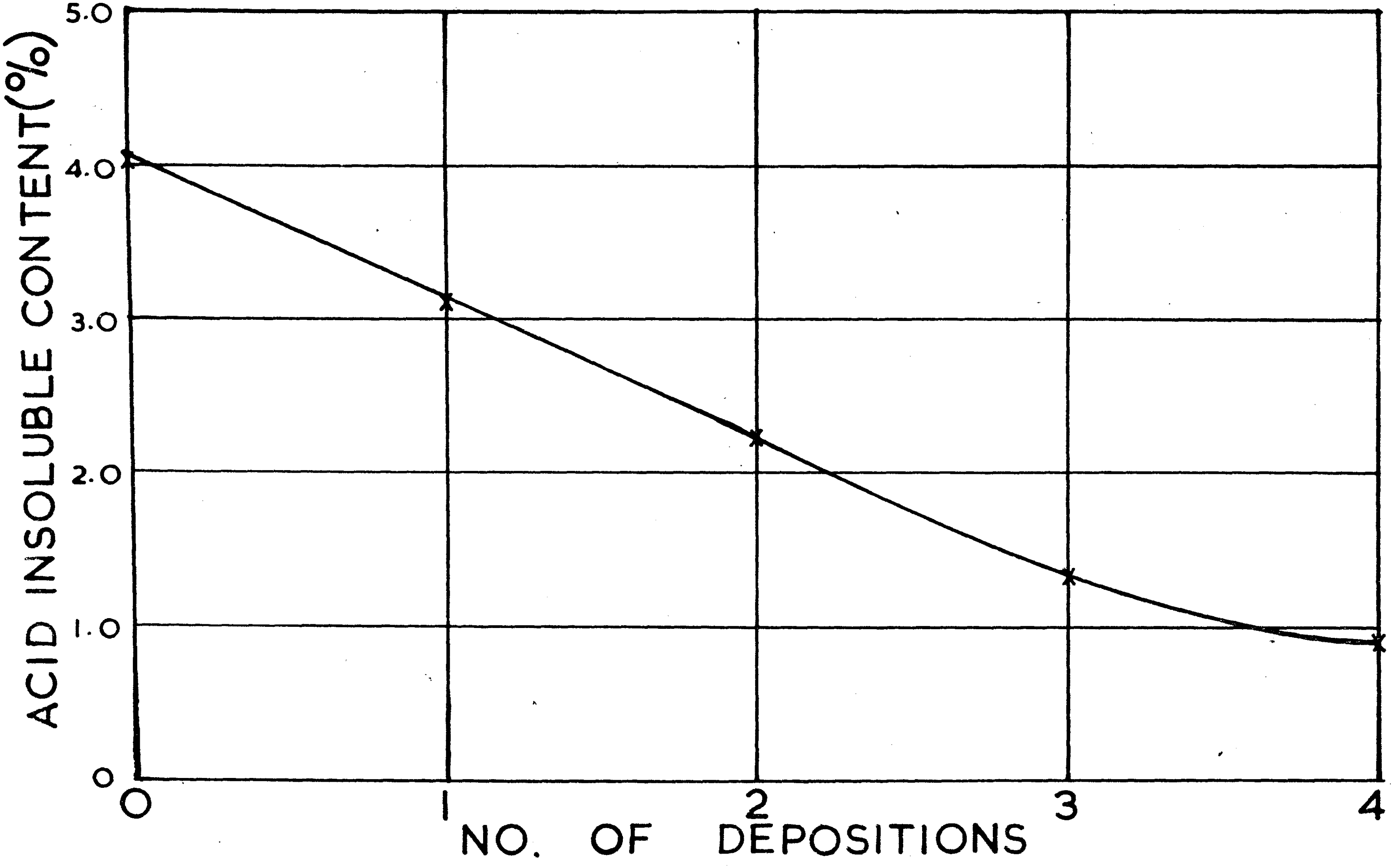

ACID INSOLUBLE CONTENT(%)
5.0
4.0
3.0
2.0
1.0
0
0
1
2
3
4
NO. OF DEPOSITIONS

FIGURE 22

since the acid-insoluble content could be reduced from 19% to 4% in these fractions by a single deposition.

In the sieve fractions containing about 4% acid-insoluble material the reduction was not so marked but repeated deposition continued to reduce the figure.

This method of repeated deposition, while successful, was difficult to carry out on the laboratory scale owing to the very great reduction in available material for each successive stage.

Attempts to obtain greater deposits by using high concentrations were not very successful since the heavy deposit broke away from the cathode.

It was found, however, that half-calcined Duror dolomite gave a much more coherent deposit and a four-stage deposition was made, as against three stages using the original dolomite.

To overcome the reduction in available material at each stage it would be necessary to find some method other than deposition on a static electrode and it is felt that a process could be evolved employing a rotary electrode system.

A suggested design is an apparatus closely resembling a rotary vacuum filter in which the suspension of dolomite would be fed into a metal tank acting as the anode. Dipping into/

into this tank would be a cathode in the form of a rotary drum. The deposited material would be removed by a scraper blade of insulating material. The dolomite suspension would be kept as such by agitators situated at the base of the tank. The overflow from the first unit would flow into a second and from there to a third etc. This would allow of continuous operation and would keep each cell working under practically constant conditions of concentration.

It would also be possible to design a cell in which the container was not live, being replaced as anode by a wire gauze screen situated at a suitable distance from and shaped to the form of the periphery of the cathode drum.

From the results obtained with the static unit, the best method of operation would be to crush and grind the dolomite to as fine a state of division as possible, half-calcine the material, suspend it in methyl alcohol at a concentration of at least 0.5g./ml. and feed this suspension continuously through a series of cells until the concentration fell to such an extent that deposition was not successful. The exhausted suspension could then be drawn off and methyl alcohol recovered.

The solid deposited on the cathode drums of the various units would be fed to a mixing vessel in which it would be again suspended in methyl alcohol and passed to a second series of cells where the same procedure would be adopted, the deposited material/

material passing to a third unit etc.

This method would involve a large plant and it might be possible to reduce this merely by re-circulating the suspension, using only one deposition cell in each stage. Fresh dolomite could be fed in to replace the amount leaving the system.

Such a process would require extensive investigation on the laboratory and pilot-plant scale before it could become industrially sound. Points which would require special attention would be:-

(1) Insulation of apparatus.

(2) Loss of alcohol by evaporation and in the deposited solid.

(3) Economical aspects.

It is possible that the eventual waste solid might be made to yield a further product by suspending it at high concentration.

The process is based, of course, on the fact that the acid-insoluble material is mainly siliceous and as such carries a negative electrical charge. Where the acid-insoluble material is not present as free silica, but perhaps as an insoluble silicate, the separation would not be possible. The Kishorn dolomite used was shown to be unsuitable, presumably for this reason, the acid-insoluble content being only slightly reduced after two depositions.

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EXPERIMENTAL SECTION

PART II - ORGANIC

A. FISH PROTEIN.

A. FISH PROTEIN.

Material.

The fish albumen used was a sample of a commercial product.

Analysis of Fish Protein.

Moisture Content(as supplied).....	10%
Ash Content.........................	7.7%
Protein Content....................	76.1% (Kjeldahl N x 6.25).

A considerable number of tests were made before a suitable method of ashing was found. The method adopted was to carbonise the material in a platinum crucible, supported in an iron crucible over a Meker burner. The carbonised material was then heated slowly in a muffle furnace to 800°C., taking three hours to raise the temperature from 300 to 800°C., so that the material could swell gradually. The material was finally ashed by heating at 800°C.

Apparatus.

The cell used for electrodialysis is shown in Figure 4. Both pairs of outer sections were used, the first having nickel and the second platinum electrodes.

A mechanical stirrer, passing through the upper opening of the centre section, provided agitation for the suspension.

The diaphragms found suitable for use with the cell were cellophane and a regenerated cellulose, used commercially as sausage skin.

The electrical circuit used was that shown in Figure 10.

Experimental Section.

In all the tests made, 4%(w/v) solutions were used, the solutions being made by mixing 4 g. of the fish protein into a cream in a mortar, transferring the material to a beaker, adding the bulk of the water and stirring for 60-90 minutes. The solution was then transferred to the centre section of the electrodialytic cell and the total volume made up to 100 ml.

After electrodialysis, the contents of the centre section were washed into a beaker, evaporated to dryness on a steam bath and finally ashed by the method already described.

In the initial tests the applied potential was kept constant but in later runs it was decided to limit the current in the cell to 60 ma to avoid heating effects.

All the experimental data and results from the ten tests made are given in Table XXVI, in which the following abbreviations are used:-

Diaphragms. C = Cellophane; S = regenerated Cellulose.
Water TC = tap water (circulated).
DC = distilled water (circulated).
DS = distilled water (static).

The first six tests were made using the nickel electrode cell and tests 7 - 10, using the platinum electrode cell.

Discussion/

TABLE XXVI.

Experimental Date from Tests 1 - 10.

Test No.	Diaphragm.	Water in outer Sections	App. Pot. (V.)	Initial Curr. (ma)	Final Curr. (ma)	Duration of Tests (mins)	Ash Content % of Electro-Dialysed Material.	Remarks.
1	C	T-C	200	5	5	60	7.1	
2	S	T-C	200	25	25	60	6.9	
3	C	D-C	200	15	10	60	6.8	
4	S	T-C	200	10	10	60	6.8	
5	C	D-S	200	250	275	35	-	Presence of nickel in centre compartment shown by test with dimethyl glyoxime.
6	S	D-S	200	20	100	50	-	As in Test 5.
7	C	D-S	200-95	10	60	60	5.74	Applied potential reduced after 40 mins. to maintain current constant at 60 ma.
8	S	D-S	200-95	10	60	60	5.99	Applied potential reduced after 25 mins. to maintain current constant at 60 ma.
9(1)	C	D-S	200-90	10	60	60		After 60 mins. the test was interrupted and the outer sections washed out and refilled with distilled water. The test was then continued for a further 30 mins.
(2)	C	D-S	200-135	20	60	30	4.03	
10(1)	S	D-S	200-95	10	60	60		The procedure in this test was identical to that employed in Test 9.
(2)	S	D-S	200-115	10	60	30	5.2	

Discussion of Results.

The ash content of the fish protein was not appreciably reduced when either tap water or distilled water was circulated in the outer compartments. During these tests the resistance was always high and did not fall during 60 minutes.

Better results were obtained when static water was used in the anode and cathode spaces but it was found that nickel electrodes were attacked, causing contamination of the material in the centre section. Platinum electrodes were, therefore, used in later tests.

Cellophane diaphragms gave a slightly greater reduction in the ash content of the electrodialysed material as compared with regenerated cellulose, all other conditions of experiment being the same.

The greatest reduction was obtained in Test 9 where electrodialysis was carried out for 90 minutes in all, draining the outer sections after 60 minutes and re-filling them with distilled water.

The reduction of the ash content from 7.1% to 4.03% represents a removal of 43.2% of the ash, while with regenerated cellulose the amount removed was 26.8%, the difference being attributed to differences in porosity and chemical structure of the two materials.

It is thought that the reason for there being no

reduction/

reduction with circulation in the outer sections was due to the small amount of material available in ionic form coupled with the low porosity of the diaphragms. This would mean that the small quantity of ions passing slowly through the diaphragm could be washed away from the electrodes and out of the cell, keeping the resistance high. This theory is supported by the fact that electrodialysis was much more successful and the resistance lower when static water was used.

The inorganic content of the fish protein is known to be mainly calcium in the form of calcium citrate, resulting from a neutralisation process. This salt is not readily soluble in water, giving a possible reason for the failure to remove more than about half of the total ash.

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EXPERIMENTAL SECTION

PART II - ORGANIC.

B. SEAWEED.

B. SEAWEED.

Introduction.

The importance of seaweed as a source of various chemicals has been known for some considerable time. Kelp-burning, to obtain iodine, has long been practised, as has the recovery of potash. Among the organic materials obtainable from seaweed are laminarin, fucoidin, mannitol, and alginic acid. Of these, alginic acid and its salts have been extensively utilised in recent years, the two main processes for extraction being the Le Gloahec-Herter process (215) and Green's cold process (216).

Electrokinetic treatment of seaweed has been more limited in its extent. A Russian patent described a systematic scheme for the consecutive separate of iodide, bromide, chloride, and alginic acid, and the eventual recovery of alkali and cellulosic material.(187) A Norwegian patent detailed a system in which alginic acid was continuously produced from seaweed by electrolytic means. Actual figures for yields and electrical energy requirements, however, seem to be lacking. (188).

REDUCTION OF ASH CONTENT OF STIPES AND FRONDS OF LAMINARIA CLOUSTONI.

General.

The reduction of the ash of various materials has been referred to previously (p. 46). In the case of seaweed the removal of inorganic material would not only mean an improvement in the quality of the organic constituents, since the material removed would be recoverable as chlorine etc., from the anode chamber and as dilute alkali from the cathode chamber. Further, both by-products are of use in the treatment of seaweed, chlorine in the bleaching and alkali in the extraction of alginic acid.

Material.

The seaweed used in this investigation was Laminaria Cloustoni, which had been dried and ground to pass a 1.6 mm. screen. Separate samples of stipes and fronds were used.

Analysis of Seaweed.

Methods recommended by Black (217) were used.

Moisture Content. This was determined by drying a 5 g. sample in an electric oven at 100°C. for six hours.

Total Ash Content. The method of dry ashing was used, 1 g. of the material being heated, at dull redness, to constant weight in a silica crucible.

Insoluble Ash Content. 1 g. of seaweed was heated in a silica crucible at dull redness for 30-45 minutes, allowed to cool and extracted with 4 x 5 ml. of hot water, decanting/

decanting off the clear liquor after each extraction through an ashless filter paper, finally transferring the bulk of the ash to the paper. The solid on the filter paper was washed with 4 x 5 ml. portions of boiling water, transferred to the crucible again and heated at dull redness to constant weight.

Soluble Ash Content. This was obtained by difference.

Analytical Results.

The analysis of the materials used gave the following results:

Stipes		Moisture	7.9%
	Dry basis	Total Ash	33.4%
		Insoluble Ash	9.1%
		Soluble Ash	24.3%
		Combustible Material	66.6%
Fronds		Moisture	6.4%
	Dry basis	Total Ash	28.0%
		Insoluble Ash	13.0%
		Soluble Ash	15.0%
		Combustible Material	72.0%

The combustible material represents the organic content of the seaweed. The constitution of the organic material in seaweed varies according to the season of the year in which it is harvested (217) and, since the material used was harvested in November, the organic content of the fronds was greater than that of the stipes.

Apparatus/

Apparatus.

The cell used for the electrodialysis of the suspensions is shown in Figures 2 and 3.

The diaphragms were of porous earthenware(Aerox $\frac{1}{8}$" CF4). The electrical circuit is shown in Figure 10.

Experimental Section.

The experimental work falls into two sections:

(a) The electrodialysis of stipes

(b) The electrodialysis of fronds.

(a) Electrodialysis of stipes.

In all the following tests, 5.000 g. (4.605 g. dry weight) of dried, milled stipes were placed in the centre compartment of the cell and 200 ml. of distilled water added. The cathode and anode sections were filled with distilled water to the overflow level. The centre compartment was stirred throughout each test. The electrodes were $\frac{1}{4}$" from the diaphragms in all cases.

The first three tests were a preliminary investigation of the effect of different voltages on the separation of the soluble inorganic material.

Test A1. On applying a potential difference of 40 volts across the cell, it was observed that the resistance dropped slowly and steadily over a period of 50 minutes before remaining/

remaining fairly constant. The current was switched off after 60 minutes. During the electrodialysis the changes in pH of the liquids in the various compartments were noted. The centre section retained its original acidity throughout, the anode and cathode compartments becoming distinctly acid and alkaline respectively. The cathode section was washed out with 5N hydrochloric acid and the amount of alkali chlorides present determined by evaporation of the recovered solution. The cathode liquid was tested qualitatively for magnesium and calcium, but no traces were found. The anode compartment was analysed qualitatively and found to contain a large quantity of chloride ions and also traces of sulphate. The alkali chlorides in the cathode section account for 10% of the original seaweed, on a dry basis.

Test A2. In this test, a potential of 50 volts was applied. The resistance was very slowly broken down and attained a constant value after 45 minutes. The contents of the cathode section were estimated as before. The contents of the centre compartment were evaporated to dryness and analysed by the procedure adopted for the original seaweed analysis. No traces of organic material were noted in the cathode section.

Test A3. An initial potential difference of 100 volts was applied in this test. The temperature of the centre compartment/

compartment rose rapidly to 40°C. in 10 minutes and the resistance dropped rapidly. The potential was then reduced to 50 volts, the temperature and the resistance remaining constant from this time. The test was continued for a further 20 minutes, making 30 minutes in all.

Test A4. A continuous flow system was fitted to the cathode compartment in an attempt to improve the separation by removing the ions from the cathode section, thus preventing an ionic "back pressure." A potential difference of 50 volts was maintained throughout the test. A constant resistance was obtained after 30 minutes, but the value was greater than that obtained in the previous tests. The test was run for 50 minutes in all.

Tests A5 and A6. Two final tests were carried out under identical conditions. A potential difference of 100 volts was applied for 20 minutes, at the end of which time the potential was reduced to 50 volts and the test terminated after a further 10 minutes. To obtain more detailed analyses of the materials transferred to the cathode and anode sections both compartments were washed out with distilled water and analysed volumetrically. The cathode solution was titrated with hydrochloric acid and the alkali content determined as potassium. The anode solution was titrated with sodium hydroxide to obtain the total acidity. The/

The hydrochloric acid present was then determined in the neutral solution by titration with silver nitrate, using potassium chromate as indicator. The difference in the estimations was due to a trace of sulphate ions.

The results obtained in all the above tests are shown in Tables XXVII and XXVIII.

The first three tests show that the best separation was obtained by applying a high potential to break down the initial resistance. This reduced the time required to obtain satisfactory separation. The effect of having a continuous flow of distilled water through the cathode section was small. The best results were obtained in Test A3 and this is attributed to a gradual clogging of the cathode diaphragm with precipitated solid, which might be either inorganic or organic in nature.

The figure obtained for the hydrochloric acid content of the anode compartment is only useful for the determination of the small sulphuric acid content by difference and as a guide to the quantity of chlorine held in solution at the anode. The chlorine liberated at the anode during electrolysis could not be determined without using an enclosed anode compartment. It may, however, be estimated by difference as the original weight of the stipes minus the sum of the weights of the recovered material, the alkali content of the cathode section/

TABLE XXVII

Test No.	Alkali Chloride in Cathode Section	Material Recovered from Centre Compartment.		
		Total Ash	Soluble Ash	Insoluble Ash
A1	10.0	-	-	-
A2	13.3	25.0	17.2	7.8
A3	7.8	7.4	1.9	5.5
A4	-	19.4	13.5	5.9
A5	-	13.2	5.8	7.4
A6	-	12.6	5.4	7.2
Original Material		33.4	24.3	9.1

All figures refer to percentage based on original material.

TABLE XXVIII

	A5	A6
	% of original material	
Recovered material from centre section	89.0	88.8
Total alkalinity of cathode section (as K)	5.15	5.47
Total acidity of anode section(as HCl)	1.96	1.96
Hydrochloric acid content of anode section	1.60	1.60
Sulphuric acid content of anode section	0.28	0.28

section and the sulphate.

On this basis, the chlorine liberated, expressed as a percentage of the original material, was 5.6% in A5 and 5.5% in A6.

The power requirements for these two tests were estimated graphically.

	Test A5.	Test A6.
Power required per lb. of dry seaweed	2.93kWh.	3.13kWh.
Alkali recovered per lb. of dry seaweed	0.052 lb.	0.055 lb.
Estimated recoverable chlorine per lb. of dry seaweed	0.056 lb.	0.055 lb.

(b) Electrodialysis of Fronds.

Three tests were carried out to find the effect of different potentials. The tests and subsequent analyses were carried out in a similar manner to Tests A1 - A3. Results are given in Table XXIX.

Test B1. The duration of this test was 35 minutes at a potential difference of 50 volts. The residue obtained on evaporation of the contents of the cathode section contained traces of organic material, thus giving a high figure for the alkali chloride content. The organic content was not identified.

Test B2. This was a short test of 10 minutes' duration and was/

TABLE XXIX.

Test No.	Alkali Chloride in Cathode Section	Recovered Material from Centre Section		
		Total Ash	Soluble Ash	Insoluble Ash
B1	6.2	23.4	10.5	12.9
B2	3.0	24.2	11.0	13.2
B3	6.1	22.8	9.6	13.2
Original fronds		28.0	15.0	13.0

All figures refer to percentage based on original material.

was carried out at a potential difference of 100 volts. The resistance dropped slowly at first and remained constant after eight minutes.

Test B3. The final test on fronds was carried out at a potential difference of 100 volts until the resistance became steady after 10 minutes. The potential was then reduced to 50 volts and the test continued for a further 20 minutes. The contents of the anode section were examined qualitatively and found to contain a large concentration of chloride ions and a trace of sulphate ions. The material recovered from the cathode section again contained a trace of organic material.

Discussion of Results and Conclusions.

In the electrodialysis of milled stipe an excellent removal of inorganic matter was achieved. The greatest reduction in the ash content was found in Test A3, in which the electrodialysed material contained only 7.4% ash as compared with 33.4% in the original. Of this remnant ash 1.9% was soluble, while the original soluble ash content of the seaweed stipe was 24.3%. In a period of 30 minutes, therefore, 78% of the total ash and 92% of the soluble ash has been removed. The removal of insoluble ash in this period was 51%.

With fronds, however, some organic material was seen to have migrated to the cathode compartment. Ash removal was not so complete, the best result being obtained in Test B3 in which the electrodialysed frond contained 22.8% ash, of which 9.6% was soluble. The original material contained 28.0% ash of which 15.0% was soluble. This represents a removal of 19% of the total ash and 36% of the soluble ash, none of the insoluble ash being removed.

The ash of seaweed is derived (218) from inorganic salts in solution in the cell sap and from cations combined with organic constituents such as alginic acid. Dillon and McGuiness (219) have shown that alginic acid is not present as such in seaweed but is combined with calcium, iron etc. Desiccation destroys the colloidal character of these salts, rendering them insoluble.

Wassermann (220) has also stated that alginic acid is present as various metal salts.

The probable course of electrodialysis is, therefore, first the removal of the dissolved inorganic salts and then, more slowly, the removal of metal ions present as relatively insoluble salts of alginic acid, fucoidin etc.

Less inorganic material was removed from frond than from stipe and it is postulated that this is because the stipe contains more inorganic material in the dissolved state and is therefore more readily electrodialysed.

No/

No reference has been found regarding the nature of the insoluble ash from seaweed but it is thought that it is most likely to contain iron and, possibly, silica.

The presence of silica would explain the partial removal of insoluble ash, since it could then be due to anodic migration of the negatively charged silica.

When frond was tested, less of the soluble ash and none of the insoluble ash was removed and, since the inorganic material is most unlikely to be radically different from that in the stipe, it is possible that some factor such as cell wall thickness or strength may hinder the removal of the inorganic ions.

In the case of calcium alignate the association of the cation with the long-chain anion is another possible source of interference with normal electrodialysis. This phenomenon has been shown to take place with sodium ions in the electrodialysis of aqueous solutions of polyacrylic acid and sodium hydroxide. (221).

In general, therefore, it can be stated that where the inorganic material which constitutes the ash of a particular material is completely or almost completely soluble, its removal by electrodialysis can be accomplished in a relatively short time. If, however, the inorganic matter is present in the form of insoluble or relatively insoluble compounds, the reduction/

reduction of the ash content by electrodialysis is very slow if not altogether impossible.

Recovery of materials from the anode and cathode chambers was of the order of 1/20 of the original weight both in the case of chlorine and of alkali. The electrical energy required was about 3 kWh. per lb. of dry seaweed or approximately 60 kWh. per lb. of chlorine and of alkali. These figures do not compare well with those obtained in the electrolysis of alkali chlorides for the production of chlorine in which the energy requirement is about 2 kWh/lb. of chlorine (222). It must be remembered, however, that the chlorine produced in the electrodialysis of seaweed is a by-product and the economics of the process would be a matter of balancing the cost of collecting the chlorine against its value, since there is no extra expenditure in causing it to be electrolysed.

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REMOVAL OF INORGANIC MATERIAL FROM MANNITOL.

REMOVAL OF INORGANIC MATERIAL FROM MANNITOL.

Introduction.

Mannitol occurs in the fronds of seaweed to an extent varying from 10% to 40% (217). It is soluble in water and can be extracted from the plant by this medium or with alcohol. In either case the extracted mannitol is heavily contaminated with inorganic salts, 40% being common.

The production of mannitol of higher purity may be possible either by electrodialysis of the extracted material or extraction of the mannitol from previously electrodialysed seaweed.

Material.

The seaweed used was L. Cloustoni frond which had been dried and ground to pass a 1.6 mm. screen.

The ash content of the original frond was found to be 35.5%.

Apparatus.

The electrodialytic cell used was that shown in Figure 5, diaphragms of regenerated cellulose being employed.

Experimental Procedure.

Extractions were carried out in a 1 litre round-bottomed flask fitted with a link stirrer and mercury seal, a reflux condenser also being provided. An electric heating mantle was used with a rheostat to control the rate of heating.

The/

The charge of fronds and solvent was refluxed for three hours, the contents of the flask then being filtered, first through nylon cloth to remove the coarser material and finally through a fluted filter paper. The filtrate was evaporated to dryness on a steam bath, the resultant solid transferred to the original flask and refluxed with methanol for a further three hours. The contents were filtered hot through a fluted filter paper, the volume of methanol reduced on a steam bath and the mannitol allowed to crystallise.

Experimental.

(1) Water Extraction of seaweed, separation of impure mannitol and subsequent Electrodialysis.

50 g. of dried frond were refluxed with 500 ml. of distilled water for three hours and impure mannitol separated as described above.

4.2 g. of mannitol were obtained, with an ash content of 70%. 1.26 g. of the impure mannitol were placed in the centre section of the electrodialytic cell and all three chambers filled with distilled water. Electrodialysis was carried out for an hour. 0.64 g. of mannitol were recovered from the centre compartment, with an ash content of 41%.

(2) Electrodialysis of frond followed by extraction of mannitol with water.

10 g. of frond were electrodialysed for two hours in the centre compartment of the cell. The treated frond was then extracted with distilled water.

The/

The ash content of the frond was found to have been reduced from 35.5% to 21.9%, a removal of 38% of the total ash.

The yield of mannitol was 0.23 g. from 7.5 g. of frond. This amount was insufficient for an accurate ash determination.

(3) Water extraction of frond and electrodialysis of extract after filtration.

50 g. of frond were refluxed with 500 ml. of distilled water for three hours.

After filtration, 100 ml. of the extract were electrodialysed in the centre compartment of the cell for one hour.

There was a negligible yield of mannitol from the electrodialysed extract.

It seemed apparent from the results obtained that mannitol was being lost from the centre compartment during electrodialysis. An electro-osmotic flow was observed during the tests and, although it is not thought that mannitol has a pronounced charge, this flow would tend to carry off dissolved mannitol to the cathode chamber together with the inorganic cations forming the ash.

To check this point two tests were carried out in which pure mannitol was electrodialysed in the cell.

(4) 2.39 g. of pure mannitol were electrodialysed in the centre section of the cell for one hour in distilled water. On completion of the test, the contents of all three compartments were evaporated to dryness. The following figures were obtained:

Wt. of mannitol initially in centre section	2.39 g.
Wt. of mannitol in centre section after electrodialysis	2.07 g.
Wt. of mannitol in cathode section after electrodialysis	0.29 g.

No appreciable amount of mannitol was found in the anode section of the cell.

The amount of mannitol carried into the cathode section was 12%.

(5) 2.50 g. of pure mannitol and 1.00 g. of pure sodium chloride were electrodialysed in the centre section of the cell for one hour in distilled water. The contents of the centre and cathode sections were collected and evaporated to dryness.

Wt. of mannitol in centre section initially	2.50 g.
Wt. of sodium chloride in centre section initially	1.00 g.
Wt. of residue from centre section	2.94 g.
Wt. of residue from cathode section	0.58 g.
Ash content of residue from centre section	24.6%
Mannitol remaining in centre section	2.20 g.
Mannitol removed to cathode section	0.30 g.
	= 12 %

Discussion.

The ash content of mannitol was reduced from 70% to 41%, a removal of 41% of the ash. ? Of the impure mannitol placed in the centre section of the cell in Test 1, only 51% was recovered. In Test 2, 0.23 g. of mannitol was obtained from 7.5 g. of electrodialsed frond as compared with 4.2 g. from 50 g. of untreated material. Practically no mannitol was obtained from an electrodialysed extract in Test 3.

These findings pointed to the fact that mannitol was being lost during electrodialysis. It is not thought likely that mannitol will have a definite charge and the loss is, therefore, probably caused by the dissolved substance being transported to the cathode chamber as a result of electro-osmotic flow. The traces of organic material found in the cathode liquids during previous tests on electrodialysis of fronds (p. 155) are thus, presumably, mannitol.

The final tests showed that mannitol was being transported to the cathode chamber. A lower percentage, 12% against ca. 50%, was removed when pure mannitol was used and the addition of sodium chloride to increase the current did not lead to a greater amount of migration.

It may be concluded that, due to the solubility of mannitol in water, removal of soluble inorganic contaminants from/

from it by electrodialysis cannot be achieved without a very considerable loss of the mannitol itself. A possible solution of the problem might be the formation of an insoluble compound of mannitol from which the soluble inorganic contaminants could be removed by electrodialysis.

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REMOVAL OF ELECTROLYTE IMPURITIES FROM ALGINIC ACID.

Introduction.

The removal of electrolytes from alginic acid is a difficult process. It was hoped that an electrodialytic treatment might prove successful.

Material.

A sample of crude, unbleached alginic acid was used and alginic acid was precipitated from the electrodialysed frond recovered from previous tests (pp. 155-6).

Analysis.

The crude alginic acid was found to contain 14.1% moisture and 78.4% alginic acid, giving a content of 91.2% alginic acid on a dry basis. The method of analysis adopted was that of Cameron, Ross and Percival (223).

Apparatus.

The cell used in the electrodialysis was that shown in Figures 2 and 3.

Experimental.

(1) 5.0 g. of crude alginic acid were suspended in 200 ml. of distilled water in the centre compartment of the cell and a potential of 100 v. applied for 40 minutes. The resistance did not decrease.

Analysis of the cathode liquid showed that the amount of alkali chlorides present was equivalent to 1.4% of the crude alginic acid.

The/

The material from the centre section was recovered by filtration and dried with hot air.

Analysis of the recovered alginic acid which had a moisture content of 14% showed the alginic acid content (dry basis) to be 92.3%

(2) 5.0 g. of crude alginic acid were suspended in 200 ml. of distilled water in the centre compartment and the potential applied for one hour, placing the electrodes closer to the diaphragms. The cathode section was analysed for alkali and it was found that the amount of alkali chlorides present was equivalent to 3.58% of the crude alginic acid.

The material from the centre compartment was recovered as before and showed the alginic acid content (dry basis) to be 96.8%.

(3) 5.0 g. of the crude acid were dissolved in 200 ml. of an alkaline solution of sodium hypochlorite (pH 8-9) containing sufficient free chlorine to bleach the resultant solution to a light straw colour. The bleached solution was then placed in the centre section of the cell and electrodialysed. The pH of the centre compartment dropped steadily and reached a value of 1 after one hour, when a gelatinous precipitate appeared.

Due to the presence of free chlorine, the resistance of the cell was low and a reduced potential had to be applied to/

to prevent excessive heating effects. This prolonged the treatment and the quality of the alginic acid recovered was very poor, presumably because of the prolonged soaking in the bleaching solution.

(4) 5.0 g. of treated stipes from Tests A5 and A6 were extracted with 100 ml. of 6% sodium carbonate and the solution bleached with a dilute sodium hypochlorite solution to a light straw colour. Alginic acid was precipitated by the addition of 2N. hydrochloric acid until a pH of 2-3 was obtained. The alginic acid was filtered on nylon cloth and then suspended in 100 ml. of distilled water in the centre compartment of the cell.

Electrodialysis was commenced at a potential of 100 v. The resistance decreased over a period of 40 minutes and then began to increase. The test was terminated after 100 minutes due to a sudden increase in the volume of the contents of the centre section.

The alginic acid was recovered by filtering on nylon cloth and drying in a vacuum oven at 40-50°C. The amount recovered was 0.471 g. against a theoretical yield (217) of 1.150 g., the percentage yield being 40%.

The acidity was determined but a high result was obtained due to the presence of traces of chlorine.

(5) A sodium carbonate extract was prepared from 20 g. of milled stipe, the extract filtered and the solution bleached/

bleached as before. Alginic acid was precipitated and treated as in the previous test.

The behaviour of the alginic acid suspension during electrodialysis was exactly similar to the previous test, the contents of the centre compartment swelling greatly after the resistance had risen.

Recovery of the alginic acid was made as previously, the final product again containing traces of chlorine, rendering the figure obtained for alginic acid unreliable.

The amount recovered was 1.970 g. which, against a theoretical yield of 4.600 g. gives a percentage yield of 43%.

Discussion.

The purity of crude unbleached alginic acid was increased by the electrodialytic removal of electrolytes.

Using bleached solutions, it was found impossible to remove the last traces of chlorine from the precipitated alginic acid since the electrodialysis had to be discontinued because of excessive swelling., This may be due to peptisation of the alginic acid suspension when only traces of electrolyte remain, leading to strong absorption of moisture.

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ELECTRODIALYSIS OF SALTS OF VARYING SOLUBILITY.

The results obtained when attempting the removal of inorganic material from seaweed and fish protein suggested that insoluble salts were more slowly electrodialysed out. To check this point, tests were made in which calcium alginate and calcium citrate were electrodialysed, since these salts were the ones probably involved.

Calcium alginate.

1 g. of alginic acid was dissolved in 750 ml. of 1% sodium carbonate solution, and the resultant solution mixed with an excess of 10% calcium chloride solution to precipitate calcium alginate. This precipitate was allowed to settle, filtered and washed free of excess calcium, testing the wash water with ammonium oxalate. The washed calcium alginate was suspended in 100 ml. of distilled water in the centre section of the glass electrodialytic cell, the outer sections filled with distilled water and a potential of 235 v. applied. Readings of current were taken every 10 minutes for 1 hour and samples withdrawn at similar periods from the cathode section. These samples were tested with ammonium oxalate for the presence of calcium. The current rose slowly from an initial value of 10 ma to a final value of 40. At the end of 1 hour, a few drops of 10% calcium chloride solution were introduced to the centre compartment. After five minutes the current had risen to 60 ma and after a further five minutes to 100.

The/

The approximate concentrations of calcium present in the various samples were obtained by comparison with standard precipitates obtained from solutions of calcium chloride of various concentrations.

A similar test was made using calcium citrate; in this case 2 g. of the solid were suspended in 100 ml. of distilled water in the centre section of the cell and electrodialysis carried out for 1 hour. The current rose from an initial value of 5 ma to a final value of 40 ma, the potential being 235 v. throughout.

The results are shown in Table XXX.

It will be seen that a very small amount of the total calcium present is removed by electrodialysis. With calcium alginate, after 1 hour, the approximate amount removed is of the order of 1-2%, and with calcium citrate about 4-5%. The effect of introducing calcium in solution is clearly shown by the rapid increase in rate of migration on adding a small amount of calcium chloride solution as was done at the 60 minute mark in the first test. The rate of migration is increased from about 4 mg./hr. to about 84 mg./hr. The calcium of calcium citrate is removed more readily than that of calcium alginate but in neither case, concentrations being taken into account, is there any comparison to the effect with calcium in solution.

TABLE XXX.

Time (minutes)		0	10	20	30	40	50	60	65	70
Concentration of calcium in cathode section (parts per million)	Calcium Alginate	0	-	6	10	12	15	20[x]	50	90
	Calcium Citrate	0	-	2	10	20	70	100	-	-

[x] Calcium chloride added after 60 minutes.

Electrodialysis of a series of calcium salts.

To obtain further information regarding the electrodialysis of salts of varying solubility, tests were made in which a number of calcium salts, chosen to cover a wide range of solubility, were electrodialysed under experimental conditions as nearly identical as possible.

The results are shown in Table XXXI.

Dialysis was carried out in the cell shown in Figure 5, using Cellophane diaphragms. Amounts of the various salts, arranged to give equal amounts of calcium, were suspended in 100 ml. of distilled water in the centre section. Distilled water was used in the outer sections. A potential of 230 v. was applied for 60 minutes. In some cases the potential had to be reduced during the test to avoid excessive heating effects caused by the heavy currents.

Of the salts used, only the chloride, bromide, sulphate and carbonate were of Analar standard, the others being of the purest form available.

Discussion of Results.

From consideration of the amounts of calcium found in the cathode space after electrodialysis it can be seen that in general the solubility of the salt controls the ease with which its constituent ions will yield to electrodialysis. It is apparent that the varying purities of the salts used have led to some slightly erratic results.

The/

TABLE XXXI.

ELECTRODIALYSIS OF CALCIUM SALTS.

Salt	Solubility (parts per hundred in water)	Amount of Calcium Transferred to Cathode Chamber(g.)	Current (amps)	
			Initial	Final
Chloride $(6H_2O)$	V.S.	0.138	0.05	0.85 *
Bromide	125(0°C)	0.126	0.03	0.64 *
Acetate	526(0°C)	0.063	0.025	0.34
Formate	16(0°C)	0.106	0.025	0.58 *
Sulphate	0.176(0°C)	0.066	0.010	0.390 *
Citrate	0.085(18°C)	0.014	0.010	0.120
Carbonate	0.0065(20°C)	0.002	0.006	0.016
Oxalate	0.0007(13°C)	0.012	0.026	0.047
Alginate	Insol.	0.006	0.013	0.235

* Potential reduced during test.

The formation of a precipitate on the cathode diaphragm was noted in all tests. This precipitate, presumably of calcium hydroxide, was found to have formed on the side of the diaphragm away from the cathode. The calcium in this precipitate should have been electrodialysed through to the cathode and its precipitation will, therefore, give rise to further uncertainty as to how much calcium would actually be removed under perfect conditions.

It can be said that the amount of calcium electrodialysed was normally proportional to the electrical energy expended although here again the presence of impurities caused one or two erratic results.

The information obtained can be considered to have given the expected result that, while a metal cation can be electrodialysed, the solubility of the salt will determine the ease with which migration will take place.

****

GENERAL DISCUSSION AND CONCLUSIONS.

Electrodialysis of Calcium/Magnesium Mixtures.

(1) It was realised that successful electrodialysis of such mixtures could not be made without the addition of some chemical reagent to cause dissolution of the inorganic material, since, even if the solid were fine enought to pass through the diaphragm under the action of an electro-osmotic flow, no separation would be achieved.

(2) The addition of electrolytes such as sulphuric acid and ammonium chloride inhibited electro-osmotic flow and the action in such cases must be regarded as being primarily electrolysis.

With sulphuric acid, calcium was found to migrate to the cathode section more rapidly than magnesium and this was attributed to the stronger adsorption of magnesium at the cathode diaphragm, a point of view supported by considerable evidence derived from work on soils.

(3) Earthenware diaphragms clogged rather quickly owing to precipitation of solid due to the change to very alkaline conditions at this point. The use of cellulosic diaphragms was not possible since it was found that hydrogen ions appeared to utilise the available pore space to the almost complete exclusion of the slower metal cations.

(4)/

(4) The best method to avoid clogging was found to be the use of a buffer solution of pH 6.5 in the cathode section to prevent a sudden change in pH at the cathode diaphragm.

(5) Ammonium chloride was used in an attempt to achieve preferential migration of magnesium to the cathode chamber. While this was accomplished, the method was not of any real value since the reagent, being a strong electrolyte, caused very high currents, which were dissipated, for the most part, in electrolysing the ammonium chloride.

(6) The use of carbon dioxide to form the soluble bicarbonate of magnesium and subsequent electrodialysis was tried with some success, especially when half-calcined material was employed. Cellulosic diaphragms could be used for such tests since the available ions were only those dissolved from the mineral.

(7) The optimum conditions which had been discovered were applied to the design and operation of an improved type of electrodialysis cell. In this, constant circulation of the anode and cathode liquids was employed to counteract polarisation and to help to break up any film of precipitated solid on the diaphragm. Buffer solution was used in the cathode space to keep precipitation to a minimum.

With this cell, a good separation was achieved when a suspension of half-calcined dolomite, which had been treated with/

with carbon dioxide, was electrodialysed.

The results of the work are in agreement with existing theories, points such as inhibition and reversal of electro-osmostic flow being encountered as expected.

Electrodeposition.

In the study of the variables affecting the electrodeposition of powdered inorganic materials from suspension in organic liquids it was found that the results were generally in agreement with previous work.

(8) With acetone only very small deposits were obtained and it appears that the presence of a hydroxyl group in the suspending medium is necessary for successful deposition.

(9) It was found that high concentrations of solids which contained a hydroxyl group gave abnormal results, a very rapid increase in weight of deposit with increasing concentration being observed.

From these two effects it seems probable that the effect of hydrogen bonding on the mutual interaction of particles/

particles in suspension may play some part in explaining the results.

(10) A drop in current was always noted during electrodeposition. This effect has been a point of difference in published work on the subject. In the present case it was thought possible that the drop in current was due to the insulating effect of the inorganic coating on the cathode, since a large drop was always found when a compact, non-porous deposit was formed.

(11) An increase in the weight of deposit was observed after efficient grinding of a material and this may be due to closer packing of the smaller particles.

In the series dolomite, half-calcined dolomite and dead-burnt dolomite, under similar conditions, the weight of deposit increased in that order. It is postulated that this effect is due to space considerations since in the half-calcined material part of the carbonate radical has been replaced by the more compact oxide grouping and in the dead-burnt form all of the carbonate has been replaced.

(12) Electrodeposition of dolomite caused no major alteration in the chemical constitution, none being expected since a double carbonate will deposit as such. The only difference observed was the reduction of the acid-insoluble content.

(13)/

(13) This fact was applied further in an attempt to produce a dolomite of very low acid-insoluble content, which would be comparable with the purer deposits found elsewhere. Duror dolomite was successfully treated in this way but Kishorn dolomite did not prove suitable. This difference can be explained by the fact that the 12% acid-insoluble content of Duror dolomite is present almost entirely as free silica while the lower acid-insoluble material in Kishorn dolomite is probably present in combined form with an overall positive charge, making separation impossible.

Reduction of ash content by Electrodialysis.

Fish protein, seaweed stipe and frond, and mannitol were electrodialysed in attempts to reduce the inorganic content.

(14) Fish protein, having an ash derived mainly from insoluble calcium citrate, did not give particularly satisfactory results.

(15) Seaweed stipe could be successfully electrodialysed although not all of the inorganic material was removed.

(16) Seaweed frond treatment was impaired by the migration of some organic matter to the cathode chamber, while the removal of inorganic material was not so effective as with stipe.

(17) Mannitol presented a different problem since it is soluble in water, and so migrated or was carried by electro-osmotic flow/

flow to the cathode section.

(18) The removal of electrolytes from alginic acid was partially achieved, the main obstacle here being the sudden swelling of the material caused by peptisation when most of the electrolytes had been removed.

Electrodialysis of salts of varying solubility.

(19) The evidence from these tests indicated that previous considerations regarding the effect of salt solubility on the progress of electrodialysis were correct.

While cations could be electrodialysed even from salts regarded as insoluble, the rate was extremely slow.

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APPENDIX I.

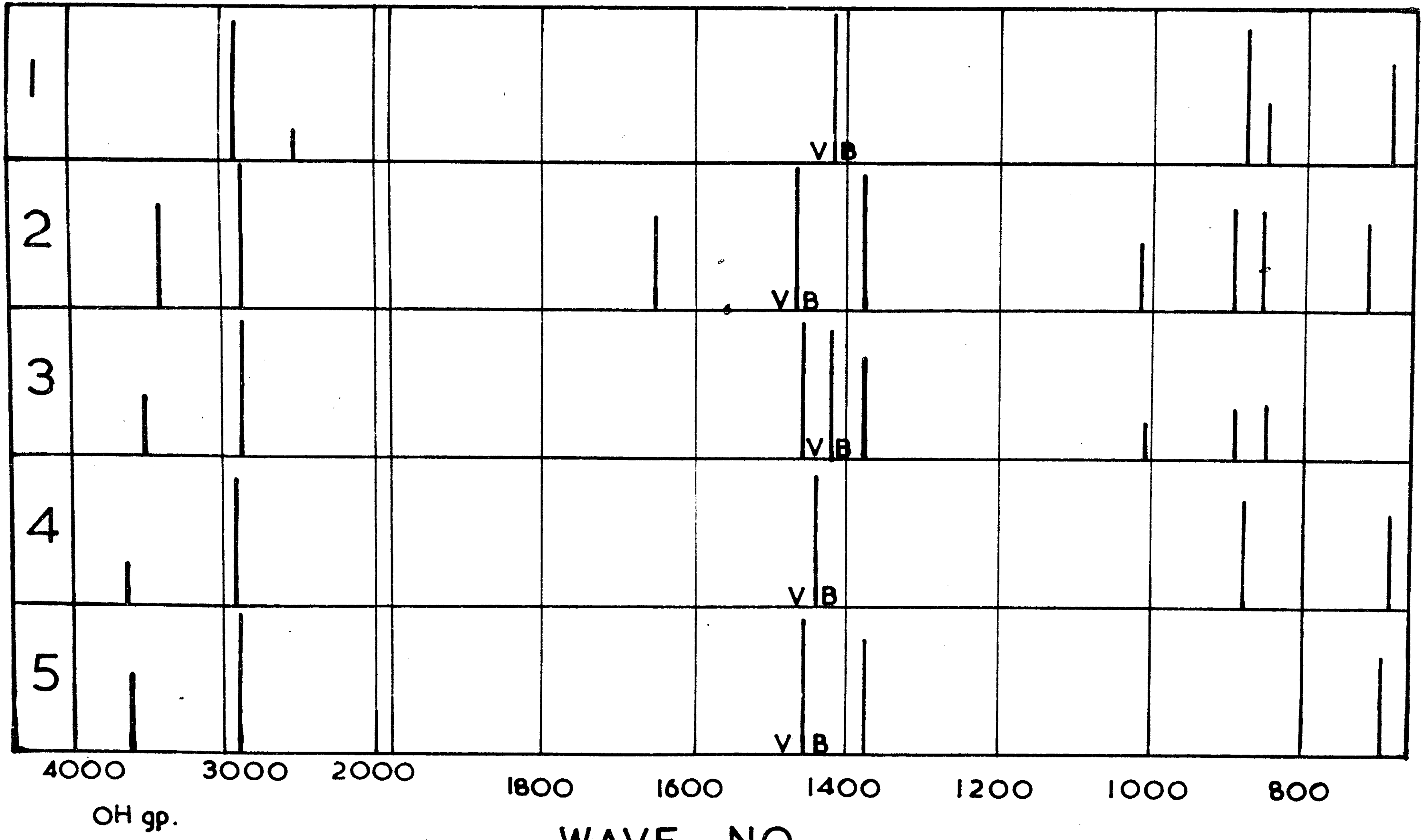
INFRA-RED SPECTRA.

Infra-red spectra of the materials used in electrodeposition (Table XXI) were made using a recording double-beam infra-red spectrophotometer. This instrument has been described by Brownlie (224).

The solids were prepared for examination by grinding them into a very fine paste with Nujol (pure liquid paraffin) in an agate mortar.

The spectra obtained are shown in Figures 23 and 24, in which the vertical lines represent absorption bands, the height being a measure of the percentage absorption.

No.	Substance.	
1	Calcium carbonate	Figure 23.
2	Heavy magnesium carbonate	
3	Light magnesium carbonate	
4	Calcium hydroxide	
5	Magnesium hydroxide	
6	Kishorn dolomite	Figure 24.
7	Duror dolomite	
8	Half-calcined Duror dolomite	
9	Dead-burnt Duror dolomite	
10	Acetone	
11	Cyclohexanone	


1
2
3
4
5
V
B
V
B
V
B
V
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V
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4000
3000
2000
1800
1600
1400
1200
1000
800
OH gp.
WAVE NO.

FIGURE 23

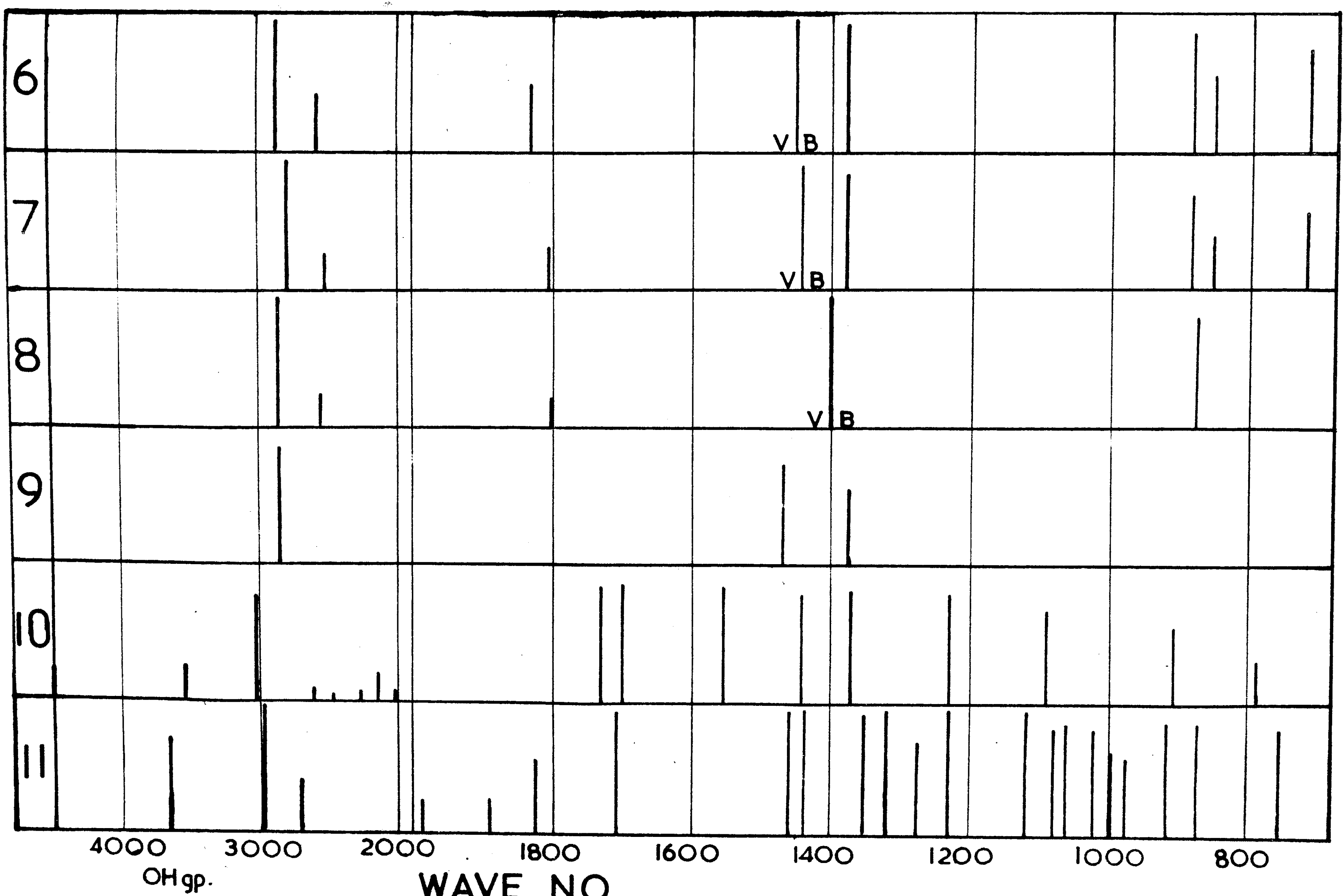
6
7
8
9
10
11
V B
V B
V B
4000
3000
2000
1800
1600
1400
1200
1000
800
OH gp.
WAVE NO.

FIGURE 24

APPENDIX II.

PHOTOMICROGRAPHS.

Photomicrographs of samples of the materials used in electrodeposition (Table XXI) were made using a Vickers projection microscope.

The degree of enlargement was ca. 1000 X, no additional enlargement being used in printing.

The results are shown in Plates 5 - 16.

Plate No.	Substance.	Remarks.
5	Calcium carbonate.	Regular rectangular crystals.
6	Calcium carbonate (ground)	Large number of crystals unchanged.
7	Heavy magnesium carbonate.	
8	Heavy magnesium carbonate(ground)	Very effective and uniform size reduction.
9	Light magnesium carbonate	Dark patches are aggregates of small particles.
10	Calcium hydroxide	Difficult to focus due to scattering of light.
11	Magnesium hydroxide	ditto
12	Kishorn dolomite	
13	Duror dolomite	
14	Half-calcined Duror dolomite	Agglomeration makes particle size doubtful.
15	Dead-burnt Duror dolomite	ditto
16	Calibration	1 division = 10 microns.

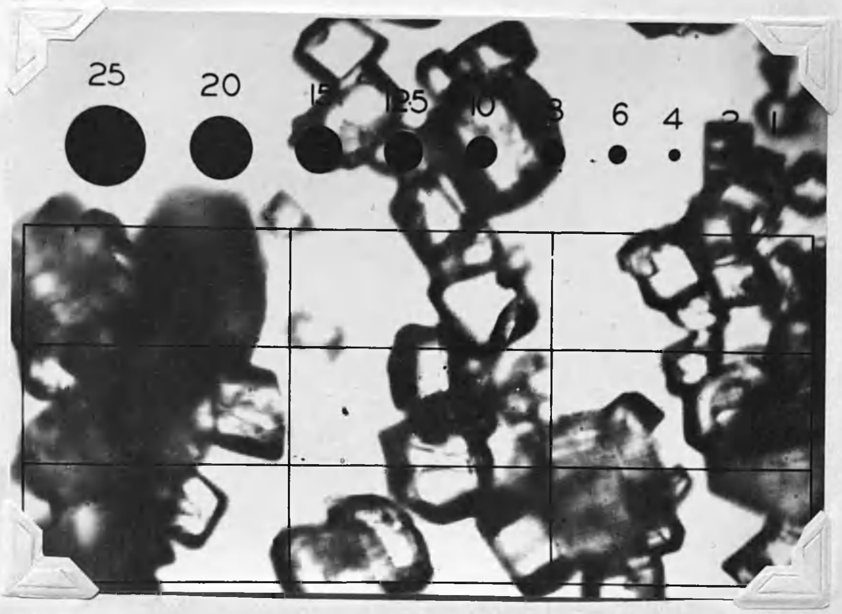

Plate 5.

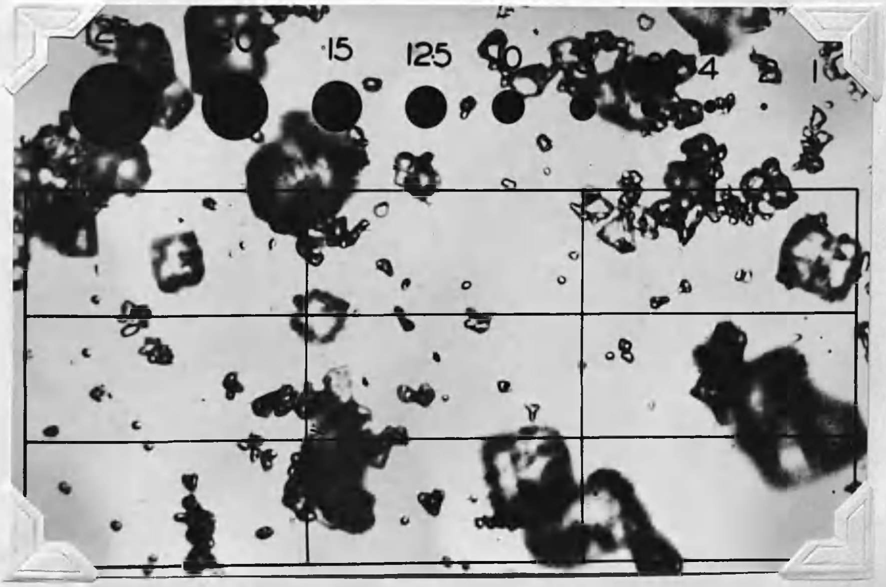

Plate 6.

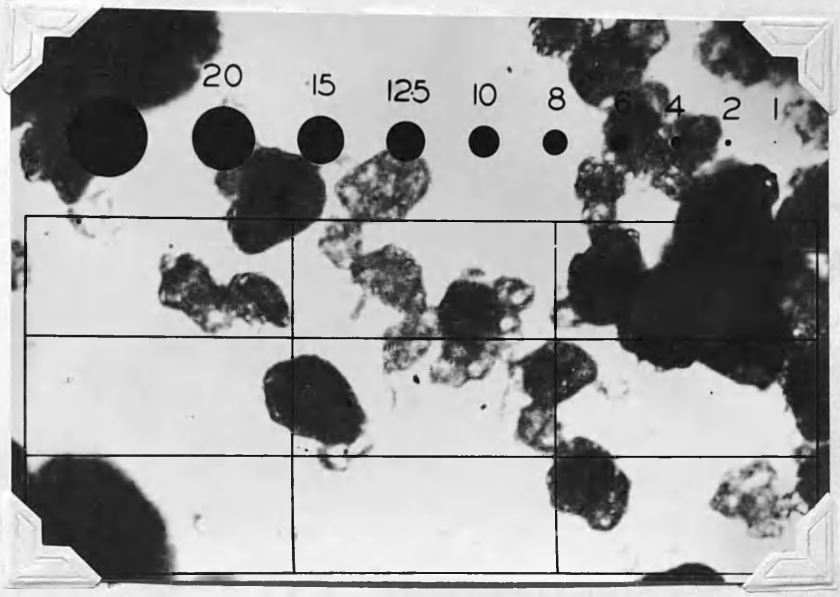

Plate 7.

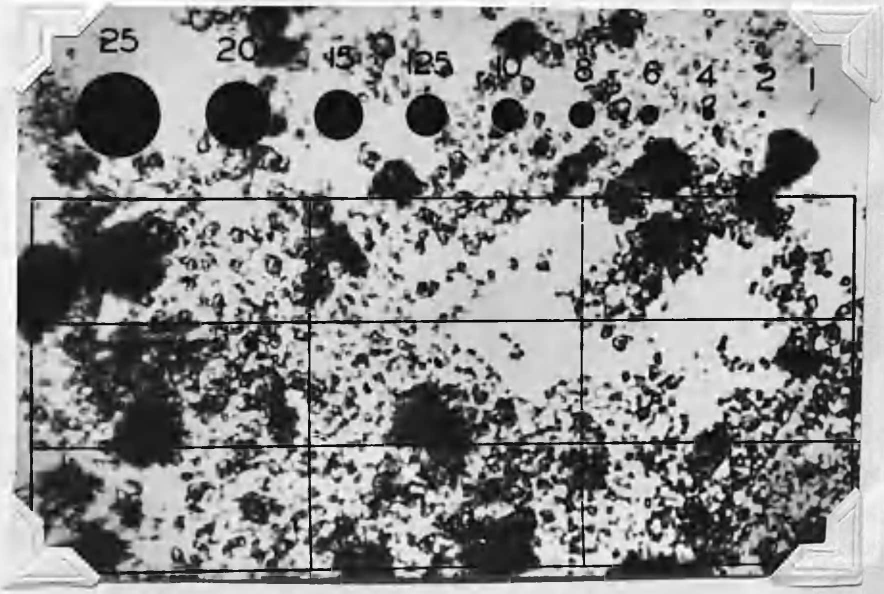

Plate 8.

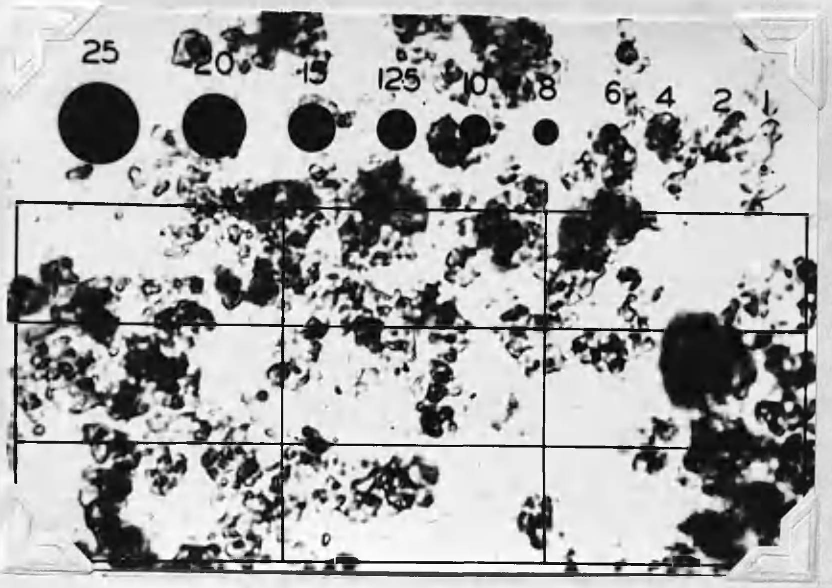

Plate 9.

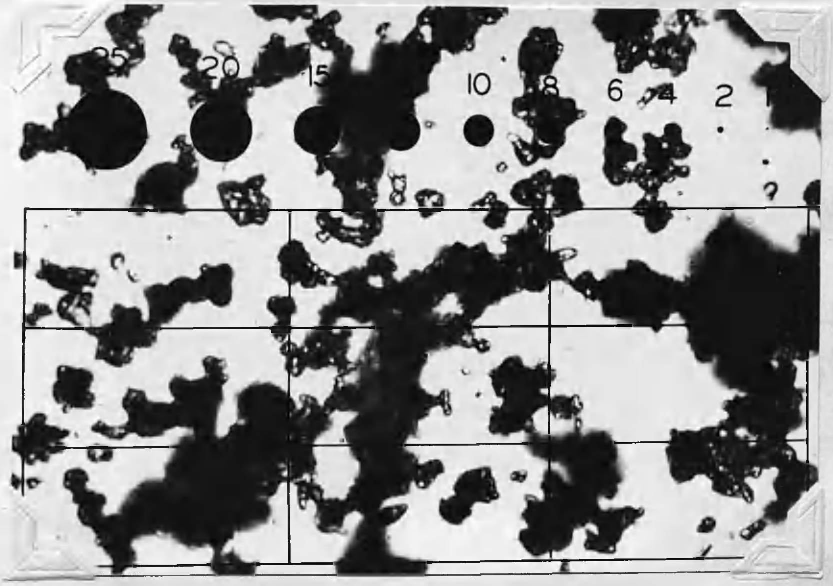

Plate 10.

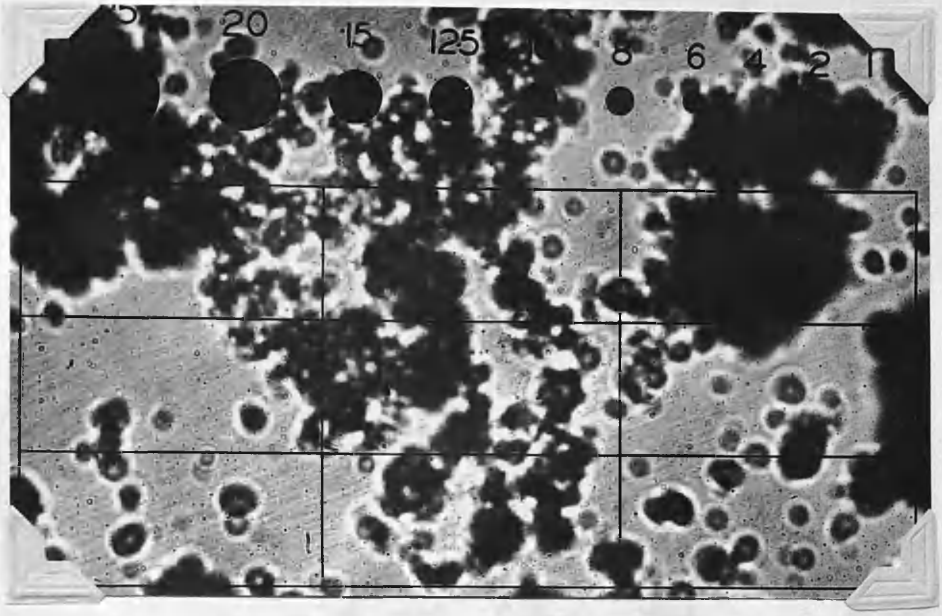

Plate 11.

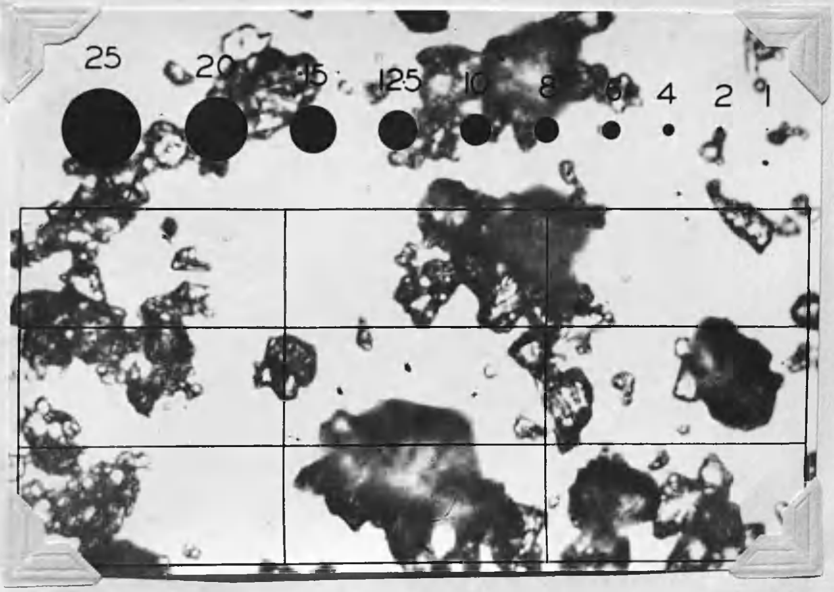

Plate 12.

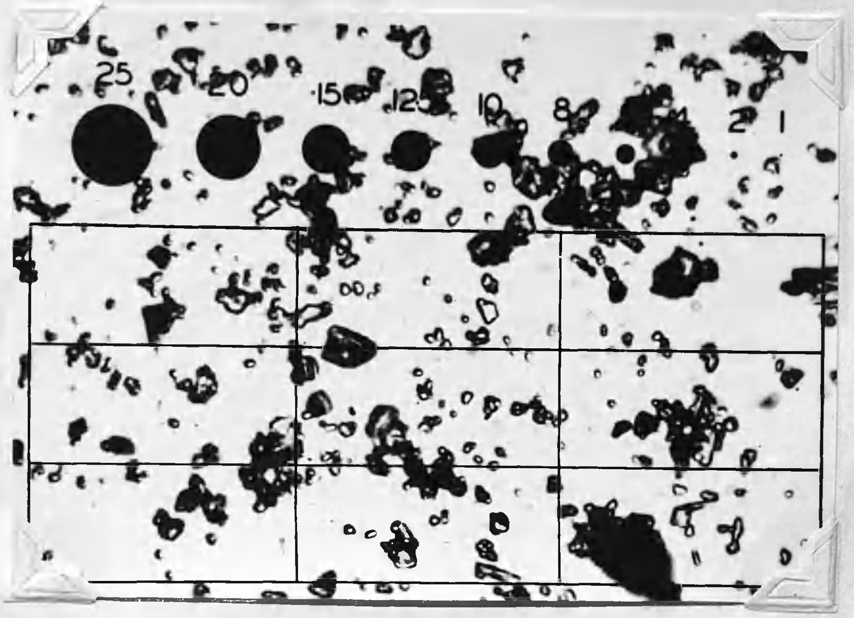

Plate 13.

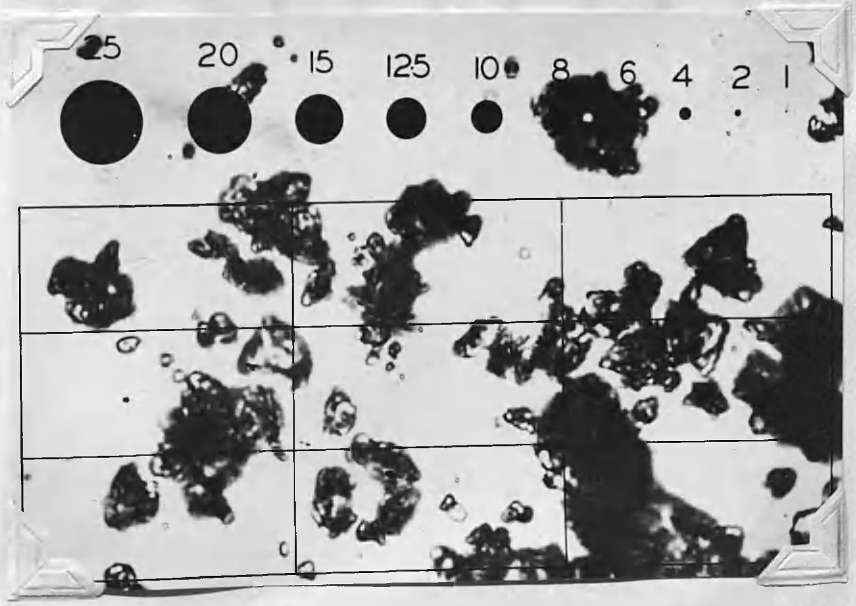

Plate 14.

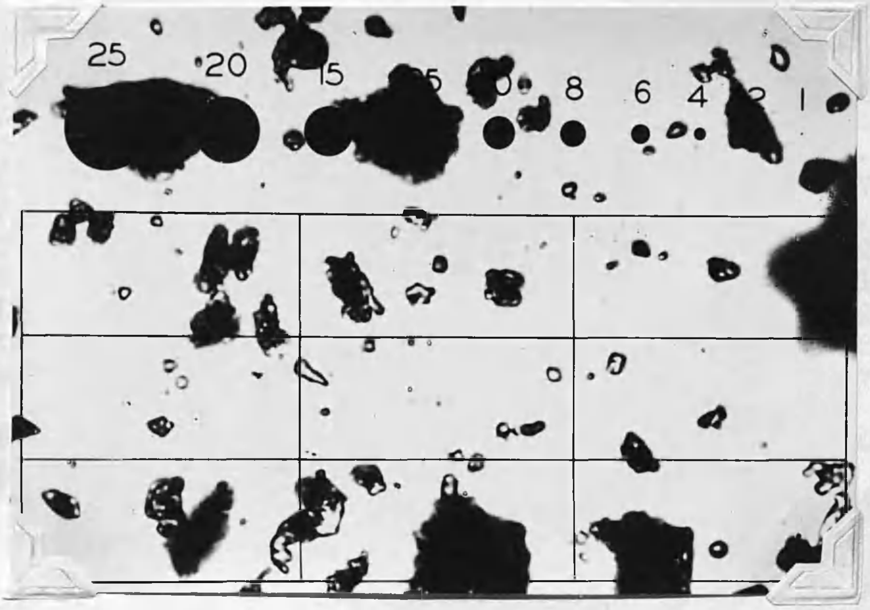

Plate 15.

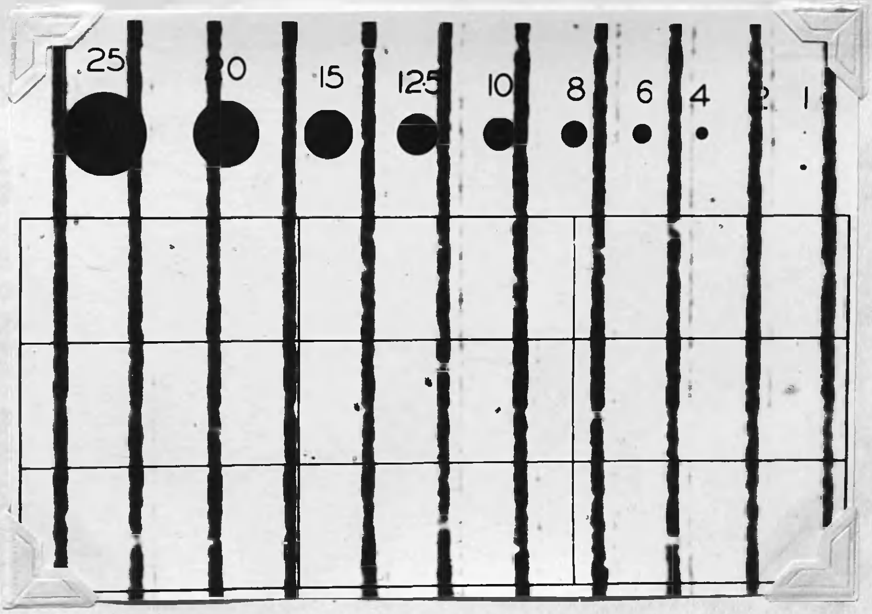

Plate 16.

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